THE FIRST SYNTHESIS OF A TRANSITION METAL COMPLEX OF CYCLOHEPTATETRAENE

By

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PARTIAL FULFILLMENT OF THE REQUIREMENTS
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1985

TO MY PARENTS

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"One takes up fundamental science out of a sense of pure excitement, out of joy at enhancing human culture, out of awe at the heritage handed down by generations of masters and out of a need to publish first and become famous."

Leon M. Lederman
The Value of Fundamental Science
Scientific American 251 #5, November, 1984.

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Abstract of Dissertation Presented to the Graduate
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Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

THE FIRST SYNTHESIS OF A TRANSITION METAL COMPLEX OF CYCLOHEPTATETRAENE

By

William Randolph Winchester

Chairman: William M. Jones
Cochairman: J. R. Sabin
Major Department: Chemistry

It is well established that cycloheptatetraene is lower in energy than cycloheptatrienylidene. To date all transition metal complexes of this ligand have been aromatic carbene complexes, no transition metal cycloheptatetraene complex has been reported.

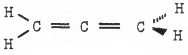
Extended Huckel molecular orbital calculated relative energies correctly show cycloheptatetraene to be lower in energy than cycloheptatrienylidene and also show that for the dicarbonylcyclopentadienyliron (Fp) complex the aromatic carbene complex is lower in energy than the cycloheptatetraene complex. This result is interpreted as resulting from a strong bonding interaction between the Fp LUMO and the cycloheptatrienylidene HOMO, which is much less strong for the cycloheptatetraene-Fp complex. Further, this result led to the choice of bis(phosphine)platinum as a metal for which the cycloheptatetraene complex would be lower in energy than the cycloheptatrienylidene complex.

The first transition metal cycloheptatetraene complex was synthesized by the generation of cycloheptatetraene in the presence of tris(triphenylphosphine)platinum and exchange to give (η^2-cycloheptatetraene)bis(triphenylphosphine)platinum. Similarly, the 1,2-η^2-4,5-benzocycloheptatetraene and the 1,2-η^2-4,5-6,7-dibenzocycloheptatetraene complexes have been synthesized. Interestingly, none of these compounds is fluxional.

A novel reaction between cycloheptatetraene and the cycloheptatetraene complex to give (7'-cycloheptatrienyl-7-cycloheptatrien-1,1'-diyl)bis(triphenylphosphine)platinum, which has been characterized by ^{1}H, ^{13}C, ^{31}P NMR spectra and an x-ray structure determination, was observed. This is the first (allene)bis(triphenylphosphine)platinum complex which has been observed to undergo this reaction. A mechanism which is consistent with this result is proposed.

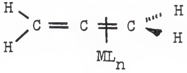
CHAPTER I
INTRODUCTION

Allenes, or 1,2-dienes, are linear compounds with a central sp-carbon bonded to two sp^2-hybridized carbons.



1

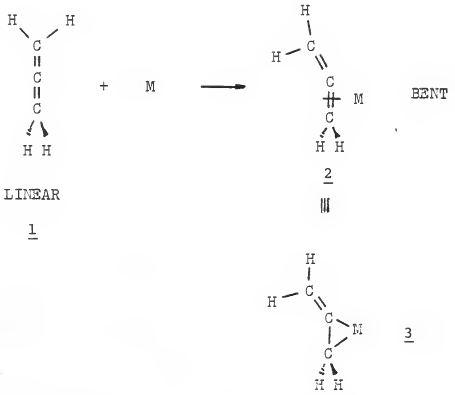
Transition metal complexes of allenes, in which the metal is bonded to one of the double bonds, form an interesting



2

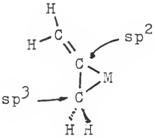
group of molecules and have been the subject of several reviews.[1-5]

Crystal structure determinations have been done for a number of allene complexes.[5] The usually linear allene is bent when complexed to a transition metal. The carbon which is not bonded to the transition metal moves away from the metal. This bending is consistent with descriptions of olefin complexes as metallocyclopropanes.

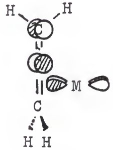


METALLACYCLOPROPANE

The metal carbon distances are not symmetrical, the MC_1 bond distance is always longer than the MC_2 bond distance. This has been attributed to the different hybridizations of C1 and C2, since increasing s-character in an orbital generally shortens the bond length.[4] It has also been attributed to the overlap of an occupied metal

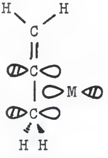


d-orbital with the orthogonal π*-orbital of the double bond which is not complexed to the metal.[6]



4

The bonding in transition metal allene complexes is usually discussed within the context of the Dewar-Chatt-Duncanson model.[7-8] There is donation from the olefin π-orbital to an unoccupied metal a_1-orbital and backbonding from an occupied metal b_1-orbital to an olefin π*-orbital. The bending of allene upon complexing to a metal has been attributed to metal backbonding.



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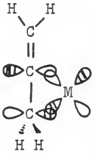

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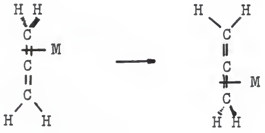
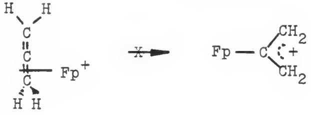
Rotation about the axis of the olefin transition metal π-bond is rapid in some allene transition metal complexes and in those cases for which rotation is rapid there is also a rapid exchange of the metal between the orthogonal double bonds. For symmetrical allenes the resulting configurations



7 8

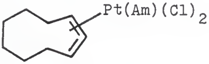
are equivalent and this exchange is called fluxional behavior.[9] Fluxional processes have been studied by several authors and as will be discussed below the mechanism appears to depend on the metal and its oxidation state.[10-13]

The fluxional exchange has been studied for dicarbonylcyclopentadienyliron (Fp) and has been shown to be intramolecular.[10] It was shown there is no loss of optical activity during the fluxional exchange of 1,2-cyclononadiene complexed to Fp. This result excludes allyl complex 10 as a possible intermediate in the Fp exchange reaction.



9 10

The work of Cope et al.[11] with platinum(II) complexes of 1,2-cyclononadiene, 11, is in direct contrast to the work with Fp. When optically pure 1,2-cyclononadiene was used to make the complex with platinum, repeated recrystallization led to a decrease in enantiometric purity. When the 1,2-cyclononadiene was released from the platinum it was found to be of lower optical purity than the starting material. Two structures were proposed for the intermediate



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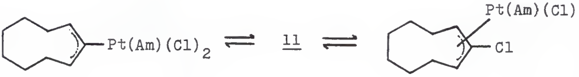
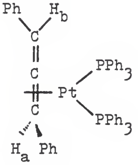


12 13

in the mutarotation, but π-allyl complex 13 is the more likely intermediate since other platinum allene complexes have been shown to rearrange to π-allyl complexes, vide infra.

Allene complexes of platinum(0) with phosphine ligands have been studied, and show no fluxional behavior.[12] The ^1H-NMR spectrum of 14 shows two signals for H_a and H_b at all temperatures, with decomposition occurring before coalscence is observed.



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As with structure and bonding, the synthesis of allene transition metal complexes has similarities to olefin transition metal complexes, with some interesting differences which can be attributed to the uniqueness of the allene. The majority of allene complexes has been prepared by exchange reactions; the allene is either added to or generated in-situ with the transition metal and displaces a ligand from the metal. For example see Figure 1.

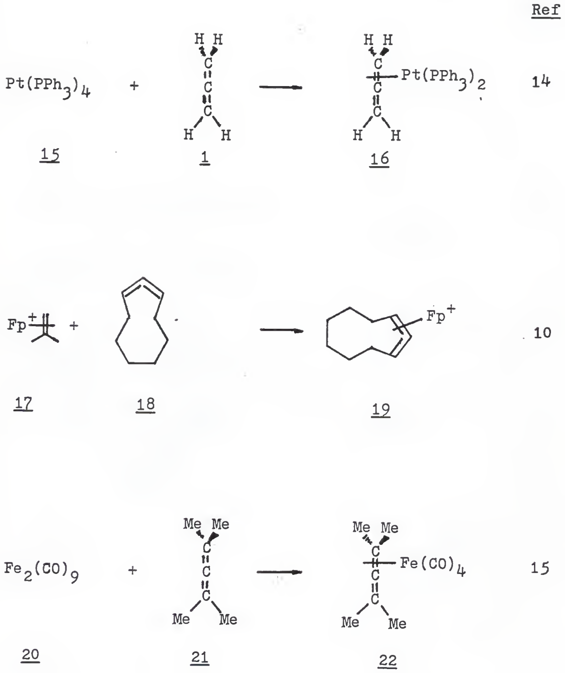
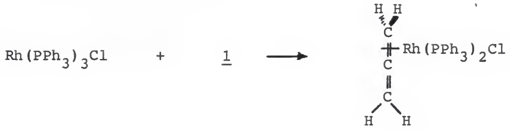


Figure 1. Synthesis of transition metal allene complexes.

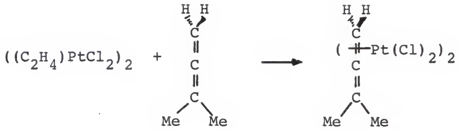
Figure 1. Continued.

Ref



14

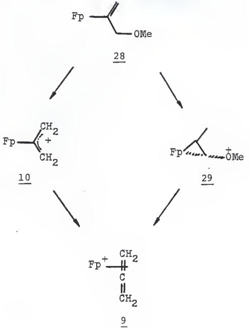
23 24



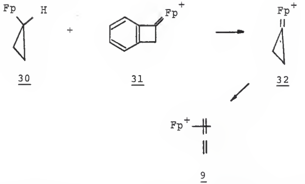
16

25 26 27

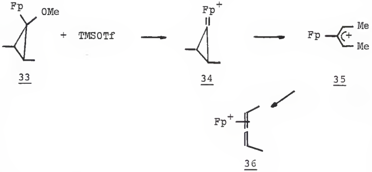
Several allene complexes have resulted from intramolecular rearrangements. Treatment of 28 with acid leads to the allene complex 9.[17] While it is possible the allyl cation 10 is an intermediate, it is most likely there is neighboring group participation of the iron.



While studying hydride abstraction from 30, it was found that the unusual reagent, 31, gave the π-complex of allene.[18] Alpha hydride abstraction gives 32, a highly strained alkylidene, which rearranges to the π-complex.

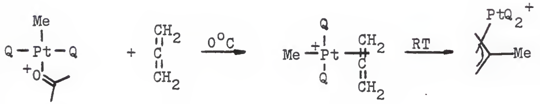


This reaction has been studied starting with resolved 33.[19] Treatment of 33 with trimethylsilyltriflate leads to the formation of optically inactive allene complex 36 The racemization was interpreted as occurring via initial formation of carbene 34, followed by opening to achiral



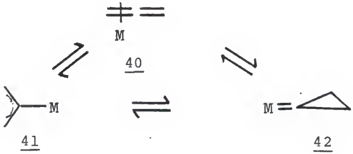
allyl cation 35 and finally rearrangement to the allene complex 36.

In what appears to be the reverse process of 35 to 36, platinum(II) allene complexes have been observed to rearrange to π-allyl complexes.[20-23] Allene displaces acetone from 37 to give an allene complex, 38, which can be isolated below 0°C. If this is allowed to warm to room temperature in solution, π-allyl complex 39 is formed.

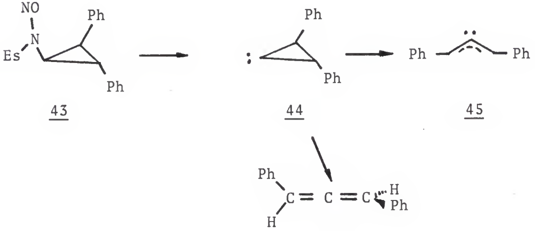


37 1 38 39

This discussion of allene complexes has led to the introduction of complexes of the general types 40, 41, and 42. The interconversion of metal complexes of this



type is of interest, but has been studied very little. However, the interconversion with no metal has been thoroughly studied. When cyclopropylidene 43 is generated from an optically active precursor, the product, 46, is the optically active allene indicating that the achiral, planar allene, 45, is not an intermediate in the reaction.[24-27]

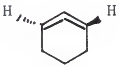


43 44 45

46

optically active

Allenes which have been incorporated into a ring have been the subject of more recent investigations.[28-29]



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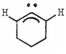
Incorporating an allene into a ring forces it to bend about the central carbon and twists the π-bonds from their usual perpendicular geometry. This raises the energy of the allene closer to the bent, planar geometry 48 which experiences little deformation on incorporation in a ring.



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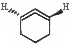
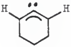
Cyclic allenes with fewer than eight carbons cannot be isolated and indirect methods have been developed to probe the structure of these molecules.

A cyclic allene has C_2 symmetry and therefore is chiral. Its planar valence isomer, 48, has C_s symmetry



C_2

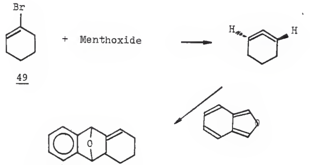
47



C_s

48

and is therefore achiral. Balci and Jones[28] have used this difference to probe the structure of the six and seven membered ring compounds. Their results show that the product of dehydrohalogenation is chiral and therefore for the six membered ring the allene, 47, is still lower in energy than its planar form. This is in accord with recent FORS

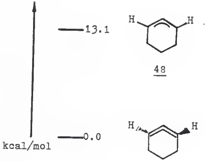


49

optically active

50

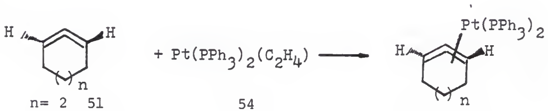
(Full Optimized Reaction Space) calculations which show the allene to be preferred by 13.1kcal/mol for the six membered ring.[29]



48

47

There are two reports of the synthesis of strained cyclic allenes complexed to transition metals in the literature. Visser and Ramakers[30] trapped the seven, eight, and nine membered cyclic allenes with 54. The



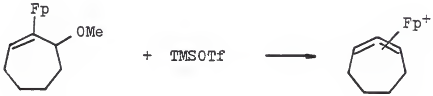
n= 2 51
3 52
4 53

54

n= 2 55
3 56
4 57

resulting π-complexes were crystalline, air stable complexes that were not fluxional.

The Fp complex of 1,2-cycloheptadiene, 59, has been synthesized by methoxy abstraction from 58.[31] This compound

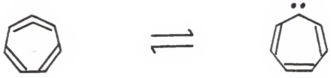


58

59

is fluxional with a 13.9kcal/mol activation barrier for the 1,2-shift.

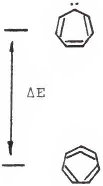
Cycloheptatetraene, 60, is a strained, cyclic allene which has been the subject of much interest.[32-36] The planar form of this allene is aromatic and this decreases the difference in energy between the planar form 61 and the allene 60.



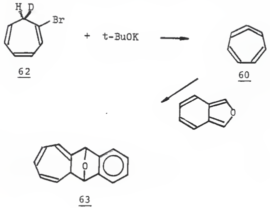
60 61

Calculations are all in agreement that cycloheptatetraene is lower in energy than its planar form. Waali,[34] using the MNDO method, has calculated the vibrational force constant matrix and normal modes for the planar form 61 and his results are consistent with the planar form 61 as a transition state connecting the enantiomeric cycloheptatetraene geometries.

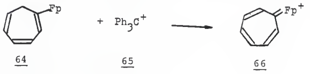
Method	ΔE	Ref
INDO	13.8	36
MNDO	23	37
EHT	28	38
STO 4-31G	15.8	39



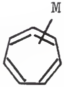
Harris and Jones [32] studied the dehydrohalogenation from optically active bromocycloheptatriene 62. The isobenzofuran adduct of cycloheptatetraene is optically active, consistent with the calculated lower energy of cycloheptatetraene relative to its planar form 61.



No transition metal cycloheptatetraene π-complex has been synthesized. But many transition metal complexes of its planar valence isomer have been synthesized. In the original work,[37] reaction of sigma compound 64 with the hydride abstractor 65 gave the cycloheptatrienylidene complex 66. The compound was sufficiently novel that an



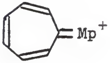
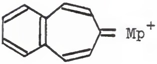
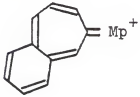
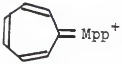
x-ray crystal structure was obtained for it and its benzannelated derivative.[38-39] The crystal structure shows unequivocally that the ligand is planar and sigma bonded to the metal. Hydride abstraction to give the carbene complex has proven to be a very general reaction and Table 1 gives some of the compounds made and the ^{13}C-NMR shift of the carbene carbon. The allene complex, 67, was not observed in any of the reactions, even as a side product.

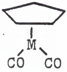


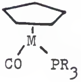
67

It was the primary objective of this research to synthesize the first transition metal complex of cycloheptatetraene. First, molecular orbital calculations were used to study the bonding in 40, 41 and 42. Then using the results of these calculations a transition metal system was chosen and the first transition metal cycloheptatetraene complex synthesized.

Table 1. ^{13}C NMR chemical shifts (ppm) of the carbene carbon in some cycloheptatrienylidene transition metal complexes.

Structure	M=Fe	M=Ru
 68	242.3	223.6
 69	265.9	244.7
 70	201	186.6
 71	278.8	256.2

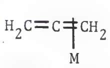
Mp= 

Mpp= 

CHAPTER II

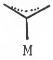
RESULTS OF EXTENDED HÜCKEL CALCULATIONS

The bonding in the transition metal complexes 40, 41, and 42 was studied using molecular orbital calculations of the extended Hückel type.[40,41] The transition metal complexes



$H_2C{=}C{=}CH_2$ / M

40



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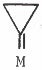
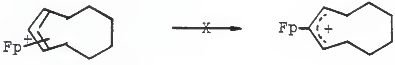


42

with M=Fp were studied first to help understand the experiments discussed in the introduction. Then the transition metal complexes with M=$Pt(PH_3)_2$ were studied because it was expected a cycloheptatetraene complex of this system could be synthesized and because it was expected that studying the bonding in a different transition metal complex for comparison with Fp complex would be useful.

The relative energies calculated by the extended Hückel molecular orbital method (EHMO) for 72, 73 and 74 are shown in Figure 2. Experiments have shown that generation of both the cyclopropylidene complex 74 and the allyl complex 73 leads to the formation of the allene complex 72, indicating that the allene complex 72 is the preferred valence isomer.[17,18] In agreement with this experimental result the allene complex 72 is calculated to be lowest in energy. Allyl complex 73 is next highest in energy, 24 kcal/mol above 72. The cyclopropylidene complex 74, is calculated to be highest in energy, 33 kcal/mol above the allene complex 72.

A minimum for the energy difference between the allene complex 72 and the allyl complex can be deduced from an earlier reported experiment.[17] There is no loss of optical purity on refluxing the optically active allene complex 19 for two hours at 80°C. If one assumes a preexponential



19

75

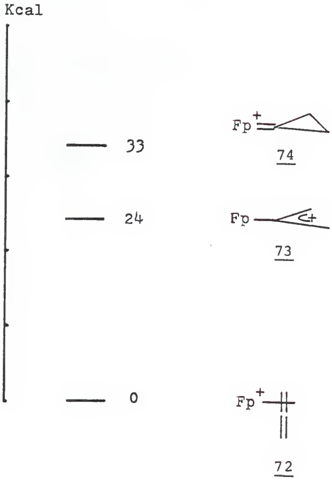


Figure 2. Relative energies of 72, 73 and 74 in kcal/mol.

term in the Arrhenius equation,[42] A, of 10^{13} and a $T_{\frac{1}{2}}$ of two hours then the calculated barrier is 30 kcal/mol. This also assumes that the transition state for racemization

$$E_a = R\, T_k^o\, [\ln(T_{\frac{1}{2},sec}) + 35.73]$$

is the allyl cation and not some intermediate in the conversion of the allene to the allyl cation.

The relative energies of allene 76, planar allene 77, and cyclopropylidene 78 were calculated for comparison with the Fp complexes. As Figure 3 shows, allene, 76, is lowest in energy, followed by planar allene 77, and highest is cyclopropylidene 78. The ordering by energy is the same for the organic molecules as for their Fp complexes. But, the differences in energy of the organic molecules are much greater than in the Fp complexes.

In order to understand this decrease in relative energy on complexing to Fp and to understand the bonding in the Fp complexes some interpretation of the EHMO calculated molecular orbitals is necessary. The interpretation of calculated molecular orbitals for organometallic complexes has been done by arbitrarily dividing the molecule into an organic fragment and a metal fragment.[43-46] The molecular orbitals from the calculation for the molecule are discussed with an interaction diagram in terms of the orbitals calculated for the fragments. This approach was used in discussing the bonding in 72, 73 and 74.

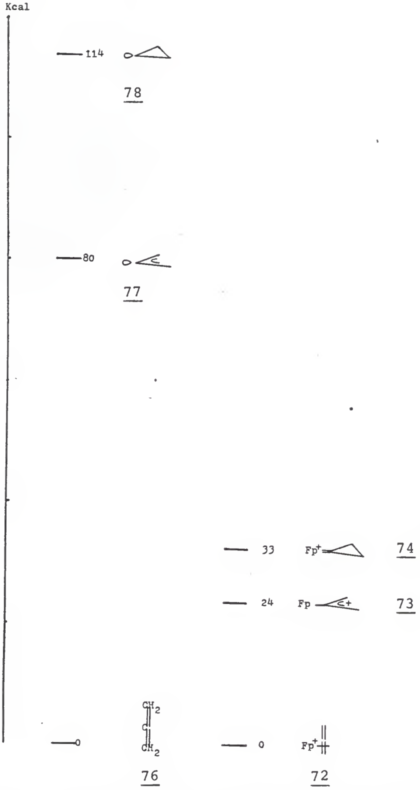
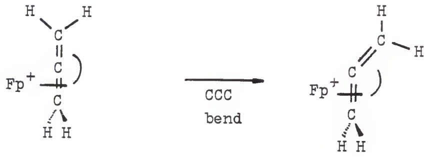


Figure 3. Relative energy of 76-78 as calculated by EHMO.

Before the calculated molecular orbitals and energies are discussed in more detail, the method used to obtain these will be described. For all the organic molecules MINDO/3 geometry optimizations were performed.[47] The resulting geometries were used for the EHMO calculations. A similar optimization could not be done with the organometallic complexes because MINDO/3 is not parameterized for transition metals. Initially the EHMO calculations on the organometallic complexes used the geometries found from optimization of the organic fragments combined with the known geometry of the metal fragment. The EHMO calculated relative energies were not compatible with the experimental results, 72 was found to be higher in energy than 73. A study of the effect of bending in the allene ligand on the EHMO total energy is shown in Figure 4. There is an



Linear

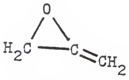
$\theta = 180^{\circ}$

Bent

$\theta \leq 180^{\circ}$

18 kcal/mol drop in total energy on bending the allene ligand from 180° to 150°, which is enough to make the allene Fp complex lowest in energy, this bend is also consistent with the known geometry of Fp allene complexes.[48]

Therefore, it was decided that using the geometries of the uncomplexed ligands would not be acceptable for the complexes. Since geometry optimizations using the EHMO method can lead to spurious results, geometries obtained from the MINDO/3 optimization of the model systems 79, 80 and 81 were used for the organic fragments in the organometallic complexes. Using this procedure assumes that the bonding in the oxygen complexes will be similar to the bonding in the Fp complexes, which is reasonable since the oxygen atom is isolobal with Fp. This procedure led to an angle of 161.3° in the geometry used for the complexed allene.



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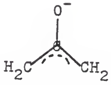

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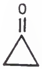

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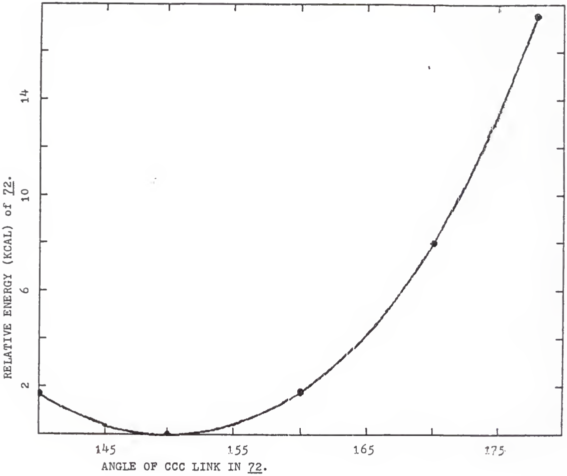


Figure 4. Affect of bending on the energy of 72.

The allene valence orbitals are shown in Figure 5. Because the allene geometry used was not linear, degeneracy of the π orbitals is lifted. While only the 1π and the 2π* orbitals are of π-like symmetry the π symbol is used for all four orbitals for ease of communication. The 2π and the 1π* orbitals have been raised and lowered in energy respectively. Note the large energy difference between the occupied and unoccupied orbitals. Allene is a stable, closed shell molecule and it will not interact with the metal fragments as strongly as will a fragment with non-bonding electrons.

The valence orbitals of the Fp fragment, 82, as calculated by the EHMO method are shown in Figure 6. Several groups have reported calculations on Fp compounds and all have found it useful to discuss their results using the Fp fragment valence orbitals.[49-50] The LUMO, 3a', is important for the strong σ-bonding with incoming ligands. The HOMO, la", is well suited for backbonding to the ligand, both energetically and geometrically.

The calculated two lowest energy conformations of 72 are upright, 72a, and bisecting, 72b, and the bisecting conformation is preferred by 20 kcal/mol. This conformation minimizes the destabilizing steric interaction between the cyclopentadienyl ring and the allene ligand and maximizes the allene LUMO overlap with the Fp HOMO. (cf. Figure 7). The experimental value for the barrier to rotation is

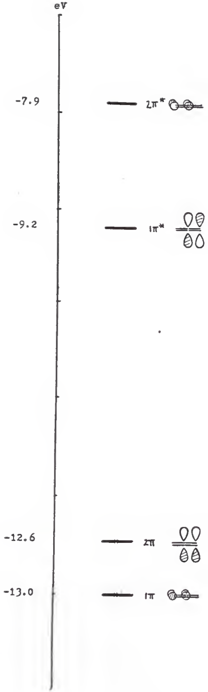


Figure 5. Allene, 76, valence orbitals.

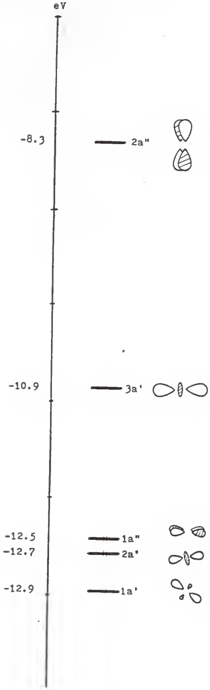
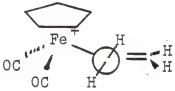
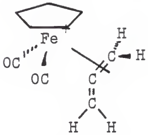


Figure 6. Fp, 82, valence orbitals.



BISECTING

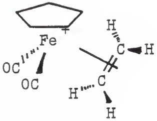
72b



UPRIGHT

72a

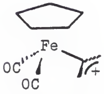
8.4 kcal/mol, which shows the calculated energy difference for 72a and 72b is probably too high.[10] The rotational barrier for the ethylene complex 83 has been calculated to be 21 kcal/mol, again a very high value. The authors state, ". . .in general extended Hückel energies are not reliable and must be viewed as indicative of trends."[49]



83

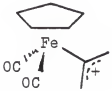
The interaction diagram for Fp with allene in the bisecting conformation is given in Figure 7. The molecule has no symmetry and the diagram is a simplified one with only the major interactions shown. The allene HOMO is a bonding orbital and much lower than the Fp 3a' LUMO. The bonding orbital resulting from this interaction is only slightly lower in energy than the allene HOMO. Similarly, a large energy difference between Fp 1a" and the allene 1π* results in a small lowering in the resulting bonding orbital.

The bisecting allyl complex 73b is calculated to be 24 kcal/mol above the allene complex 72 and 3 kcal/mol lower than its upright isomer 73a. From the valence orbitals of the allyl fragment 77, shown in Figure 8, it is apparent the HOMO, a_1, is a non-bonding orbital. The LUMO, a_2, is of the correct symmetry for π-backbonding



BISECTING

73b



UPRIGHT

73a

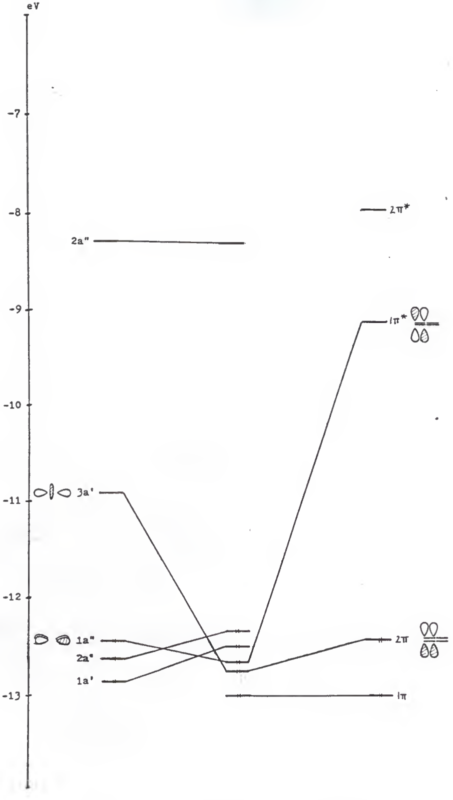


Figure 7. Interaction diagram for 72.

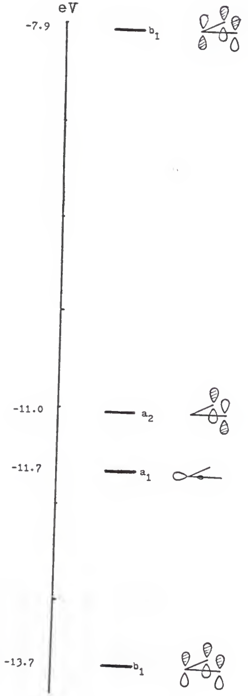


Figure 8. Allyl fragment valence orbitals.

but a node at the central carbon leads to a small overlap with other fragments and little interaction.

Most striking in the interaction diagram for 73, shown in Figure 9, is the lack of change or interaction in the a_2 orbital of allyl fragment 77. Next, there is a bonding orbital formed by the virtual Fp 3a' orbital and the occupied allyl a_1 orbital. Finally, there is a stabilizing interaction of the allyl b_1 orbital with the Fp 1a' orbital. Notice that the bonding orbital resulting from the allyl a_1 orbital and the Fp 3a' orbital is lowered by almost 2 eV. The allene 2π orbital interaction with the Fp 3a' orbital results in only a .5 eV lowering (cf. Figure 7). The decrease in relative energy of 76 and 77 on complexing to Fp appears to be due to the different ligand-HOMO, Fp-LUMO interactions.

The Fp-cyclopropylidene, 74, is the highest in energy of the Fp complexes, 34 kcal/mol above the Fp allene complex 72. The valence orbitals of the cyclopropylidene fragment, shown in Figure 10, are as one would expect. The HOMO, a_1, is a non-bonding orbital, associated with the lone pair of the carbene. The LUMO, b_1, is of the correct symmetry for backbonding.

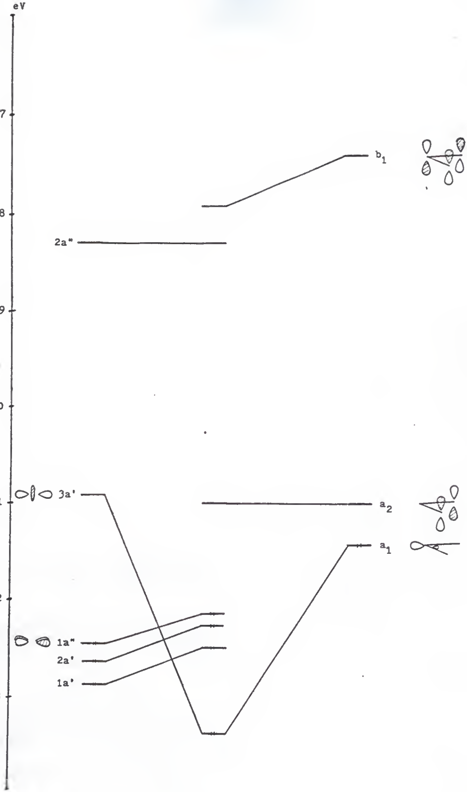


Figure 9. Interaction diagram for 73.

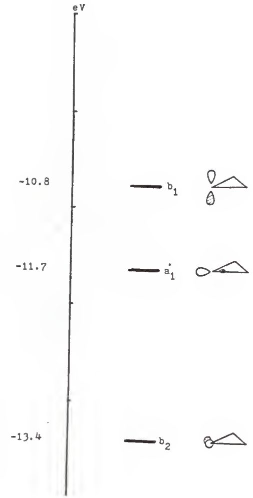
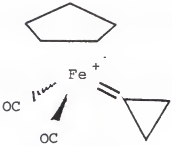


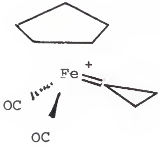
Figure 10. Cyclopropylidene valence orbitals.

The upright conformer 74a is calculated by EHMO to be lower in energy than the bisecting conformer, 74b, by 5 kcal/mol. The low difference in energy of the two conformations is the result of two opposing affects. In the upright conformation π-backbonding is strongest and in the bisecting conformation the steric repulsion between the cyclopentadienyl ring and the cyclopropylidene ligand is smallest.



UPRIGHT

74a



BISECTING

74b

From the interaction diagram for 74a, shown in Figure 11, it is apparent the strongest interaction is between the cyclopropylidene a_1 orbital and the Fp 3a' orbital; the σ-bond formation. As in the Fp allyl complex this σ-interaction is worth almost 2 eV. There is also a stabilizing interaction resulting from backbonding from the Fp 1a" HOMO to the b_1 LUMO of 78. This backbonding accounts for the greater stabilization of the cyclopropylidene 78 relative to the planar allene 77 on complexing to Fp.

Since the acyclic allenes are known to be bent when complexed to Fp, an allene which has been incorporated in a ring should be less strained when complexed to a metal than when free. At the same time EHMO calculations (vide supra) predict the allyl geometry to be closer in energy to the allene when complexed to Fp. These are opposing effects; the first will increase the difference in energy between the complexed allene and the second will decrease the difference. The relative magnitude of the two effects will determine the size of the ring necessary to make the Fp allene complex equal in energy to the Fp allyl complex. The six memebered ring allene 84, its allyl isomer 85 and 86 and their Fp complexes were therefore studied.

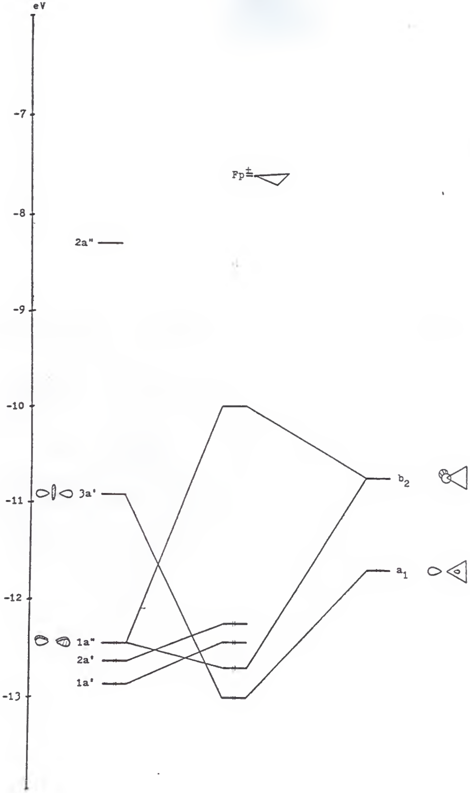
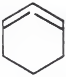
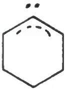


Figure 11. Interaction diagram for 74.



84



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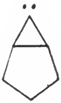


86

The geometries of the uncomplexed valence isomers 84, 85, and 86 were optimized using MINDO/3 and the EHMO calculations were done on the optimized geometries, the resulting calculated relative energies are shown in Figure 12. The cyclic allene 84 is calculated by EHMO to be lower in energy than its allyl isomer by 40 kcal/mol and is 70 kcal/mol lower than bicyclocarbene 86. These relative energies are smaller than those for 76, 77 and 78 following the expected trend. Experiment has shown the allene to be the preferred geometry, but the next accessible geometry and electronic state have not been unambiguously assigned.[28,29]

The geometries for the EHMO calculations on the Fp complexes were obtained by optimizing the corresponding oxides 87, 88 and 89 with MINDO/3. The EHMO calculated relative energies, shown in Figure 18, place the Fp allyl

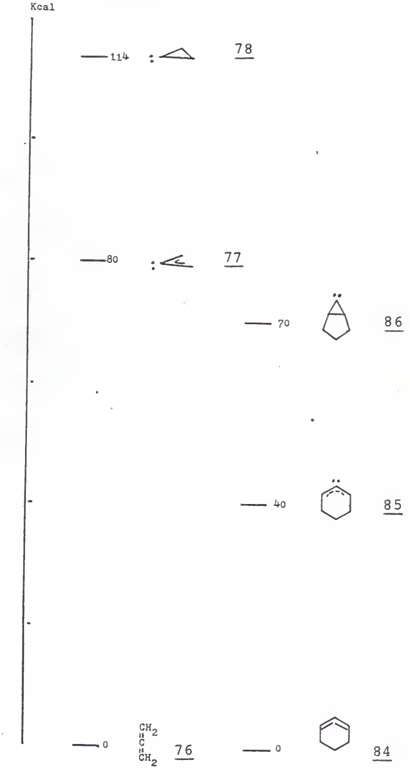


Figure 12. Relative energies of 84-86 as calculated by EHMO.

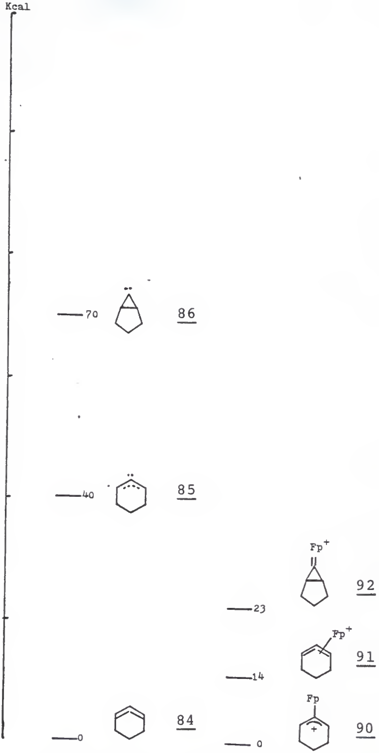
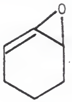


Figure 13. Relative energies of 90-92 as calculated by EHMO.



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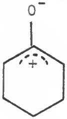

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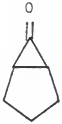


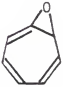
89

complex 90 lowest in energy, 14 kcal/mol below the Fp allene complex 91. The bicyclo(3.1.0)hexane carbene complex 92 is highest in energy, 23 kcal/mol above the allyl complex 90. While these results corroborate intuitive expectations, they must await experimental verification.

Finally, the cyclic-conjugated seven membered ring analogues 93, 94, and 95 were studied. Recall that 93 has been shown to be the preferred valence isomer by both experiments and calculations using the MNDO,STO-3G and STO 4-31G methods.

The geometry of 93, 94, and 95 was optimized using MINDO/3 and the EHMO calculation was then performed using the MINDO/3 geometry. Consistent with the earlier results, the cycloheptatetraene, 93, was lowest in energy 29 kcal/mol lower than 94 .^{36,37,39} Highest in energy, 94 was found to be 51 kcal/mol above cycloheptatetraene.

The Fp complexes were studied next. First the geometry of 96, 97, and 98 was optimized using the MINDO/3 program. Then EHMO calculations were done replacing the oxygen with an Fp fragment. The EHMO calculated total energies, shown in Figure 15, place the cycloheptatrienylidene complex 100 lowest in energy with the Fp cycloheptatetraene complex 99 next, 37 kcal/mol higher in energy and 101 highest, 39 kcal/mol higher in energy. NMR experiments and a crystal structure determination show 100 to be the preferred valence isomer, in agreement with the EHMO results.$^{37-39}$ There is no experimental evidence for the relative energies of 99 or 101 to 100.



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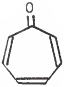

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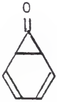

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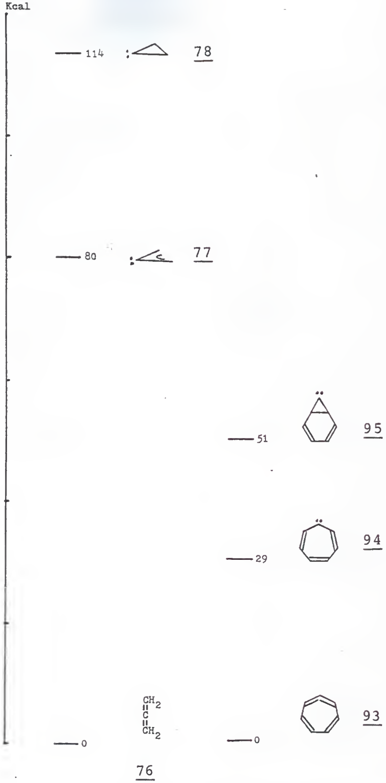


Figure 14. Relative energies of 93-95 as calculated by EHMO.

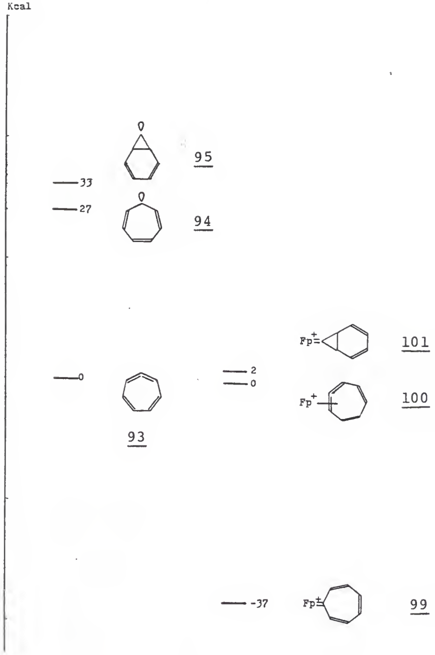
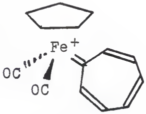


Figure 15. Relative energies of Fp complexes 99-101 as calculated by EHMO.

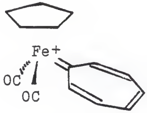
The explanation for the preference for 99 relies on our earlier results. Recall that allyl fragment 77, was found to be 80 kcal/mol above allene, 76, in energy. But, for the Fp complexes cycloheptatrienylidene, 94, was found to be only 24 kcal/mol higher in energy than cycloheptatetraene 93. The non-bonding allyl HOMO has a much stronger interaction with the Fp 3a' LUMO than does the bonding allene HOMO. For the cyclic-conjugated systems the non-bonding HOMO of 94 has a stronger interaction with the Fp 3a' LUMO than does the HOMO of 93 and the uncomplexed molecules are much closer in total energy, only 29 kcal/mol different. Therefore, one could expect that complexing to Fp would lower the energy of 94 sufficiently to make it lower than 93.

The energy difference for the upright and bisecting conformations of 100 was calculated by EHMO as 9.3 kcal/mol, with the bisecting conformation, 100b, preferred. This is



UPRIGHT

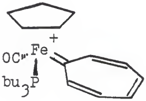
100a



BISECTING

100b

in agreement with the crystal structure determination which found the cycloheptatriene ring parallel to the cyclopentadienyl ring. The rotational barrier for 102 has been determined by D-NMR studies to be 9.7 kcal/mol, fortuitously close to the calculated barrier for 100.[51]



102

With the completion of the study of the Fp complexes, a new metal fragment was chosen for study, the primary criterion for the choice was experimental evidence which might indicate the metal complex of 93 would be lower in energy than the complex with 94. Bis(triphenylphosphine)-platinum has been used to form complexes of several reactive olefins,[30,52] so it was decided to study this metal system using the same organic fragments as in the Fp study. Trends in the relative energy as well as qualitative changes in the bonding were studied.

The relative energies of 103, 104, and 105 were calculated using the EHMO method. For the calculations phosphine was substituted for triphenylphosphine and the organic fragment geometries were the same as in the Fp calculations. The substitution of phosphine for triphenylphosphine has been used by several authors[49,50] and other than the steric differences it is assumed that the relative energies are not affected by the substitution.

The EHMO calculated total energies show 103 to be lowest in energy. Complexes 104 and 105 are of similar energy and are higher in energy than 103 by almost 55 kcal/mol. Comparison of these calculated relative energies with those for the uncomplexed molecules 76, 77 and 78 show the relative stabilization to be 25 kcal/mol for the allyl complex 104 and 60 kcal/mol for the cyclopropylidene complex 105. It is also apparent the bis(phosphine)platinum complexes are significantly different from the Fp analogues and an explanation for the difference would be useful. Interaction diagrams for 103, 104 and 105 will be used to study the bonding in these molecules.

The valence orbitals of bis(phosphine)platinum, shown in Figure 17, are very different from those of Fp even though the HOMO and LUMO are of the same symmetry. The HOMO of 106, b_2, is high in energy, 0.7 eV higher than the Fp HOMO. The LUMO of 106, 3a', at -6.5 eV, is too high for a strong interaction; it is 4.4 eV higher than the Fp LUMO. There would be no σ-interaction with 106, but a combination of the $1a_1$ and $3a_1$ orbitals lead to a σ-interaction when complexes are formed.

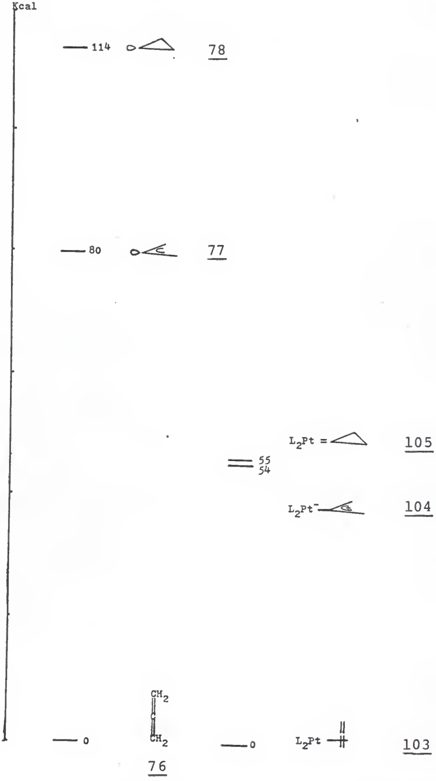
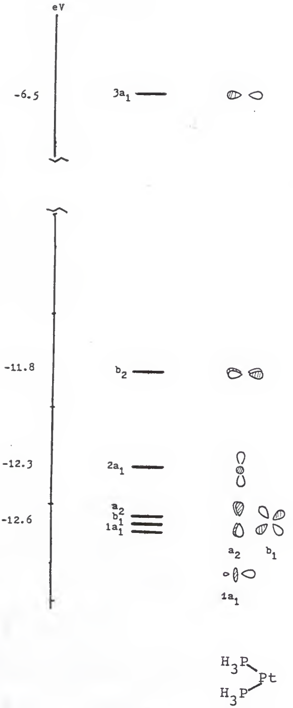


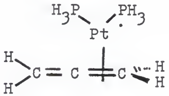
Figure 16. Relative energies of platinum complexes 103-105 as calculated by EHMO.



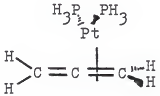
106

Figure 17. Valence orbitals for bis(phosphine)platinum fragment 106.

Lowest in energy of the three valence isomers, the allene complex with bis(triphenylphosphine)platinum, is a known compound. NMR experiments are in agreement with a crystal structure determination showing the in-plane geometry, 103i, to be preferred over the perpindicular geometry, 103p.[14] No rotational barrier has been reported; presumably decomposition occurs before rotation. The calculations are consistent with this, the square planar geometry, 103i, is lowest in energy and the calculated difference in energy is 41 kcal/mol.


IN-PLANE

103i


PERPINDICULAR

103p

An interaction diagram for the in-plane geometry, 103i, is shown in Figure 18. The bis(phosphine)platinum b_2 orbital interacts with the allene $1\pi^*$ orbital to form a bonding orbital in the complex. It is the lack of a comparable interaction in 103p which leads to a large

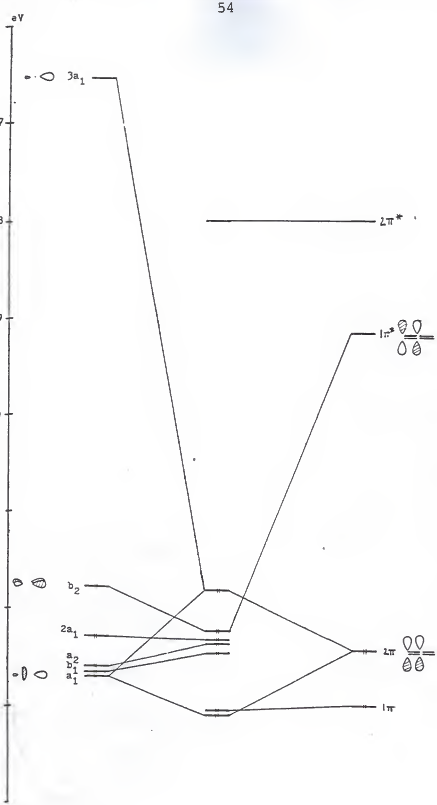
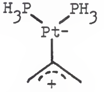


Figure 18. Interaction diagram for 103i.

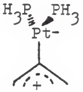
rotational barrier. There is also a stabilizing interaction between the $1a_1$ and $3a_1$ orbitals of bis(phosphine)platinum and the allene 2π orbital.

Next highest in energy is 104, calculated to be 54 kcal/mol above 103. Recall that the LUMO, the a_2 orbital, of the allyl fragment has a node at the central carbon, making this a poor ligand for metal backbonding. The calculated lower energy conformation is the upright 104a, with the plane of the allyl group perpindicular to the plane of the bis(phosphine)platinum. The energy difference between 104a and 104i is small, 4 kcal/mol.



IN-PLANE

104i



PERPINDICULAR

104a

The interaction diagram for 104a is shown in Figure 19. There is no change in the energy of the allyl a_2 orbital in the complex, as expected since this orbital has a node at the carbon bonded to platinum. The only stabilizing interaction is between the $1a_1$ and $3a_1$ orbitals of bis(phosphine)platinum and a_1 of the allyl fragment.

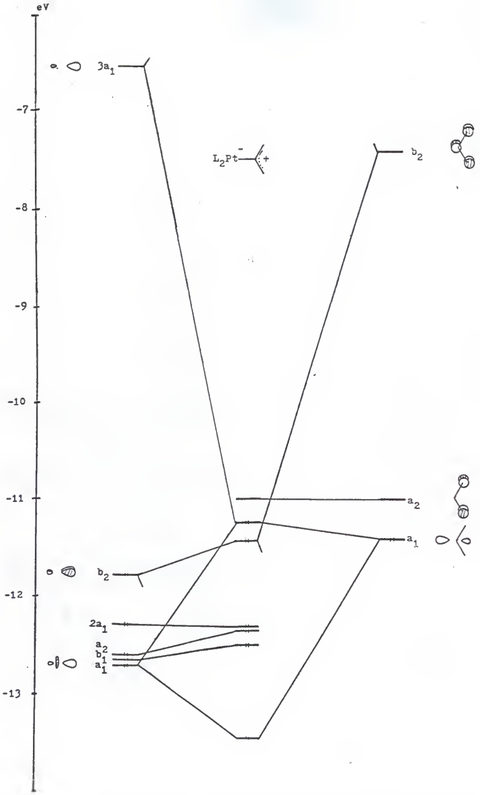
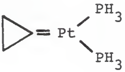


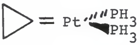
Figure 19. Interaction diagram for 104p.

Highest in energy and last to be considered is the cyclopropylidene complex 105. This is a Pt(0) carbene, of which there are no examples in the literature. The perpindicular conformation 105p is calculated to be lower in energy than the bisecting conformation. The energy difference for the two conformers is high, 18 kcal/mol.



IN-PLANE

105i



PERPINDICULAR

105p

The interaction diagram for 105p is shown in Figure 20. As in the allyl system, 104, there is a stabilizing interaction between $1a_1$ and $3a_1$ of bis(phosphine)platinum and the cyclopropylidene $a_1$orbital. There is also back-bonding from the platinum b_2 orbital to the cyclopropylidene b_2LUMO. The decrease in the relative energy fo the allyl fragment and the cyclopropylidene fragment on complexing to platinum is due to this.

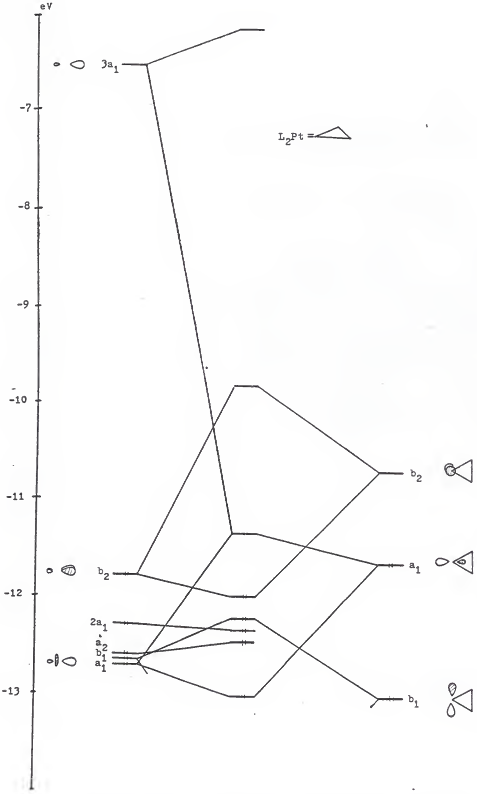


Figure 20. Interaction diagram for 105p.

To summarize the results for the bis(phosphine)platinum complexes, the allene complex is lowest in energy. The cyclopropylidene and allyl complexes are of similar energy, 55 kcal/mol above the allene complex. From the interaction diagrams this is attributed to the high energy of the virtual $3a_1$ orbital of bis(phosphine)platinum.

As in the Fp series, the bis(phosphine)platinum complexes of the six membered ring systems 107, 108, and 109 were studied. The EHMO calculated relative energies are shown in Figure 21. Interestingly the allene complex 107 is found to be lowest in energy. This is in contrast with the Fp system in which the allyl complex was lowest in energy. An attempt to make the platinum allene complex 107 has failed, but this is most likely due to the extreme conditions necessary to generate the allene.[30]

To complete the calculations with bis(phosphine)platinum, the cyclic conjugated systems 110, 111, and 112 were studied. As shown in Figure 22, the EHMO calculations place 110 and 111 at similar energies and 112 36 kcal/mol higher in energy. This is consistent with our results for the acyclic systems 103, 104 and 105. The allyl fragment was stabilized 25 kcal/mol relative to the allene fragment on complexing to platinum. Now, the cycloheptatrienylidene fragment has been stabilized 30 kcal/mol relative to the cycloheptatetraene fragment on complexing to platinum.

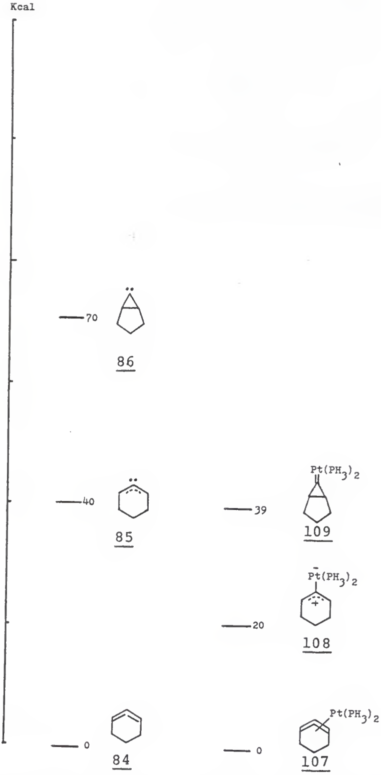


Figure 21. Relative energies of platinum complexes 107-109 as calculated by EHMO.

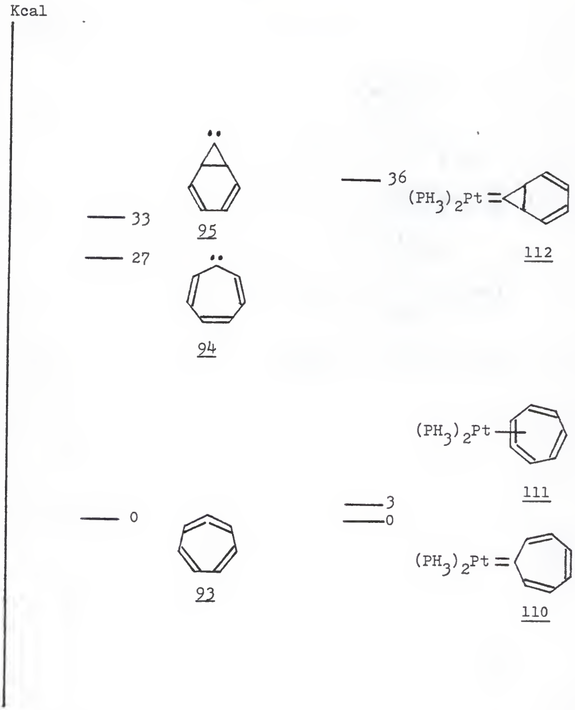
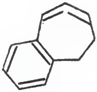


Figure 22. Relative energies of platinum complexes 110-112.

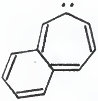
While at this level of theory an energy difference of 3 kcal/mol is not significant, the comparison of this result with that for the Fp complexes clearly shows the shift favoring the cycloheptatetraene complex with bis(phosphine)platinum. This is consistent with the experimental results. In the next chapter the first synthesis of a transition metal cycloheptatetraene complex is reported.

CHAPTER III
EXPERIMENTAL RESULTS

The EHMO calculations placed the cycloheptatetraene complex 110 at approximately the same energy as the cycloheptatrienylidene complex 111. Previous calculations had shown that annelation of a benzene ring at the (4,5) position as in 113 favored the allene form over the carbene form relative to the non-benzannelated valence isomers.[53]

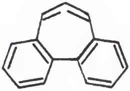


113

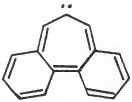


114

Similarly, annelation of benzene rings at the (4,5) and (6,7) positions had an even greater effect. The bis(triphenylphosphine)platinum complex of 115 was therefore the first cycloheptatetraene complex synthesized.

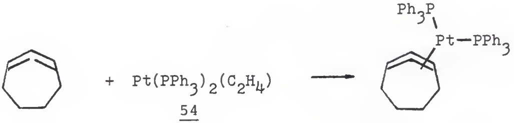


115



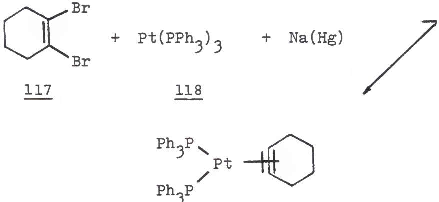
116

Visser and Ramakers have reported in a communication that the generation of 1,2-cyclophetadiene in the presence of (ethylene)bis(triphenylphosphine)platinum, 54, gave the 1,2-cycloheptadiene complex 55 but they reported no experimental details.[30]



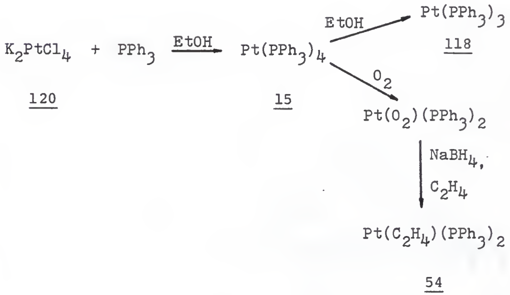
51 54 55

Bennet and Yoshida have reported that generation of cyclohexyne in the presence of tris(triphenylphosphine)platinum, 118, gave the cyclohexyne complex, 119, and reported a detailed experimental procedure.[54] Tris(triphenylphosphine)-

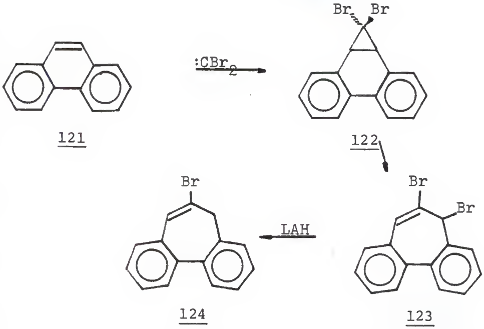


117 118 119

platinum was chosen as the trapping reagent because of the greater amount of experimental detail available for its use as a trapping agent and because it was available in higher yield than 54 from the common precursor 120.

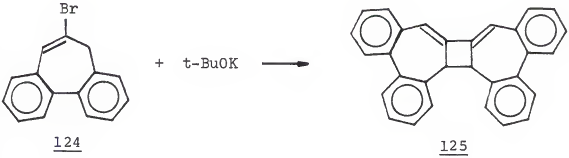


Dibenzocycloheptatetraene, 115, had never before been generated. Typically, dehydrohalogenation is a high-yield means of generating strained allenes and bromoalkene 124 was chosen as the precursor to the dibenzocycloheptatetraene for this reason. The synthesis of the bromoalkene precursor followed the method of Allison as is outlined below.[55] Addition of dibromocarbene to phenanthrene gives norcaradiene derivative 122. Thermolysis of 122 at 160°C for 30 minutes leads to disrotatory cyclopropyl ring opening and formation



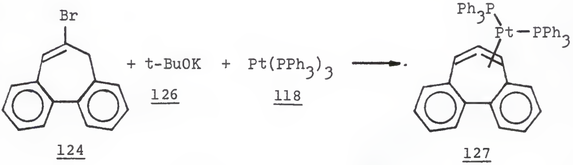
of the dibromocycloheptatriene derivative 123. Reduction of 123 to 124 is the lowest yield step in the synthesis. Lithiumtriethylborohydride, tri(n-butyl)tinhydride, sodiumborohydride, and lithium aluminum hydride were tried, but only lithium aluminum hydride gave 124 which could be readily purified, although low in yield.

Since the dibenzocycloheptatetraene, 115, had never before been generated, the reaction of 124 with potassium tert-butoxide in the absence of a trapping agent was studied.



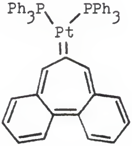
This reaction gave the allene dimer 125, as the only isolated product. Only one regioisomer is formed and its regiochemistry cannot be assigned from the spectra. However, based on the regiochemistry of the dimerization of other cyclic allenes it is assigned as above.[56]

The [1,2-η^2-4,5-6,7-dibenzocycloheptatetraene]-bis(triphenylphosphine)platinum complex, 127, was synthesized in 67% yield by the slow addition at 0°C of bromoalkene, 124, to a THF solution of 126 and 118. The assignment of the

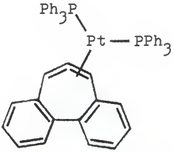


structure rests on ^{1}H, ^{13}C, and ^{31}P NMR data (cf. Figures 23 to 27) and the elemental analysis. As will be shown, comparison of the NMR shifts of the allene carbons and the phosphorous atoms of 127 with the analogous atoms in the known (1,2-cyclononadiene)bis(triphenylphosphine)-platinum complex, 57, provides strong evidence for its structure. Due to the symmetry of the carbene complex, 128,

H_1 is equivalent to H_3, C_1 is equivalent to C_3, and P_1 is equivalent to P_2, while for the allene complex 127 all these atoms are non-equivalent. The observed non-equivalence of all these atoms shows that the product cannot be the carbene complex 128, and is consistent with the allene structure.



128



127

The ^{1}H-NMR data for the dibenzocycloheptatetraene complex 127 and 1,2-cyclononadiene complex 57 are summarized in Table 2 along with the reported data for 1,3-diphenylallene complex 14. The non-equivalence of the hydrogen atoms is consistent with the assignment as an allene π-complexed to a metal. Notice that for the allene bis(triphenylphosphine)-platinum complexes many of the coupling constants to hydrogen

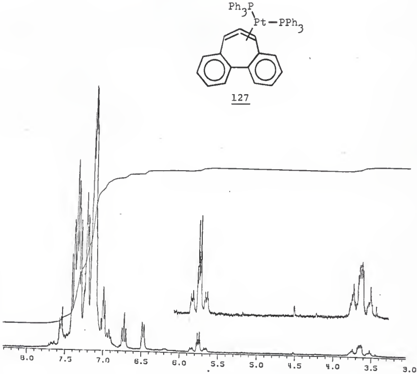
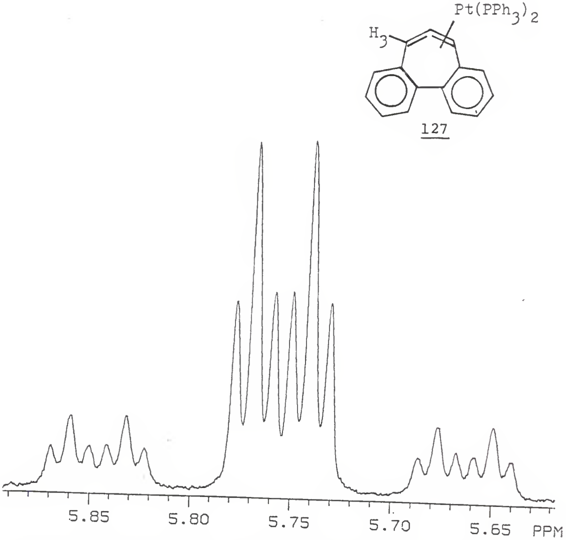


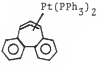
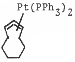
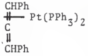
Figure 23. ^{1}H NMR spectrum (300MHz) of 127.



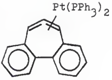
127

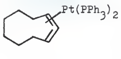
Figure 24. Expansion of ^{1}H NMR spectrum of 127 showing only H_3.

Table 2. ^1H NMR data for allene complexes 127, 57, and 14.[a,b]

	 127	 57	 14
H_1	3.48	2.4	3.75
$^2J_{PtH}$	70.8	66	65
$^3J_{PH}$	--	--	5.5
$^3J_{PH}$	--	--	9.5
$^4J_{HH}$	(2.8)	--	3.0
H_3	5.71	4.95	5.82
$^3J_{PtH}$	54.6	74	--
$^4J_{PH}$	8.4	11	12.5
$^4J_{PH}$	2.8	--	--
$^4J_{HH}$	2.8	--	(3.0)

[a] All spectra were recorded in $CDCl_3$.
[b] Chemical shifts are in ppm and coupling constants are in Hz.


127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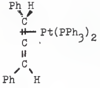
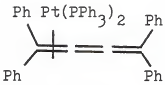
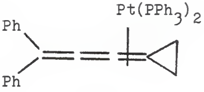

14

cannot be determined. In fact the H_3-platinum coupling constant was not reported for 1,3-diphenylallene complex 14. Otsuka et al. state the resonance was broad and the platinum coupling could not be seen.[12] For all the allene complexes studied the hydrogen resonances were broad and of low intensity, making interpretation of the ^1H-NMR spectra difficult.

Before this work was started no ^{31}P NMR data had been reported for allene complexes of bis(triphenylphosphine)-platinum. But, the chemical shifts and coupling constants of the phosphorous nuclei for several olefin complexes had been reported and recently White and Stang reported ^{31}P NMR shifts for butatriene complexes 129 and 130.[57] These are included in Table 3 for comparison with the phosphorous spectra of the allene complexes. The non-equivalence of the



129



130

phosphorous nuclei in the allene complexes is not consistent with a carbene structure, while the chemical shifts and coupling constants are consistent with the assignment as an olefin π-complex.

The ^{13}C-NMR spectra of the allene complexes 127 and 57 are very complicated. With no symmetry and 51 carbons, there is the potential for a spectroscopist's nightmare, especially if one adds long range platinum and phosphorous coupling which can lead to even more signals. Luckily, the chemical shifts of the three carbons of the allene moiety are at unusual regions of the spectrum and do not overlap with any other signals. While the ^{13}C-NMR spectra of several bis-(triphenylphosphine)platinum complexes have been reported, one author reported no coupling constants[57] and the other reported platinum, but no phosphorous coupling.[59] Thus, the first complete spectral data for the ^{13}C-NMR of

Table 3. ^{31}P NMR data of some (olefin)bis(triphenylphosphine)platinum complexes.[a]

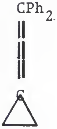
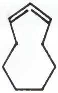
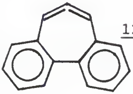
Olefin	Complex	P_a	$^1J_{PtP}$	P_b	$^1J_{PtP}$	$^2J_{PP}$	Ref.
$CH_2=CH_2$	54	32	3660				58
$CH_3-C\equiv C-CH_3$	131	19.7	3590				58
$CPh_2=C=C=CPh_2$	129	29	3416	26	3664	37	57
	130	29	2996	25.5	3550	23	57

Table 3. continued.

	57	33.8	3307	29.9	3216	48.8
	127	29	3208	27.5	3145	28

[a] Chemical shifts are in ppm and coupling constants are in Hz.

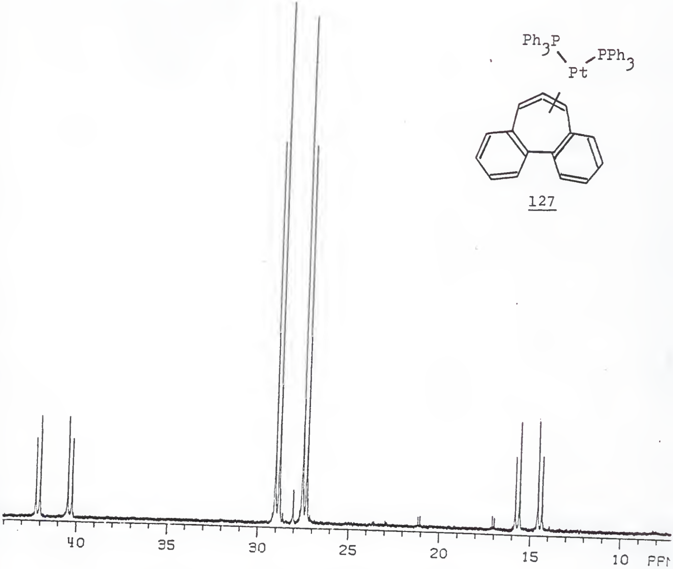
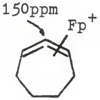


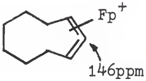
Figure 25. ^{31}P NMR spectrum of 127.

bis(triphenylphosphine)platinum olefin complexes is reported in Table 4.

Perhaps the most unusual chemical shift in the ^{13}C-NMR spectrum is that of the central allene carbon, which is found at very low field, at about 160 ppm it is consistent with the formulation as an allene complex, since uncomplexed allenes show a resonance for the central carbon at 200 ppm[60] and in all cases there is a shift to higher field on complexing olefins to a metal. The resonance of the central carbon in the iron allene complexes 19 and 59 is 150 and 148 ppm, respectively.[31]



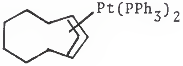
59

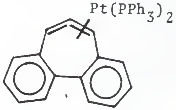


19

In attempting to reproduce Visser and Ramakers'[30]work it was found that the insertion product, 133, formed on mixing 1-bromocycloheptene and 118. The insertion of platinum into carbon halogen bonds has been reported previously and is useful for forming carbon-platinum sigma bonds.[61,62]

Table 4. ^{13}C NMR data for allene complexes 57 and 127.[a,b]

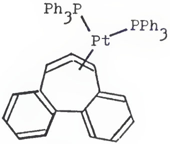




	57	127
C_1	33.8	29.5
$^2J_{PC}$	6.33	5.43
$^2J_{PC}$	38.6	52.2
C_2	161.6	164.4
$^2J_{PC}$	10.1	9.6
$^2J_{PC}$	52.3	62.9
$^1J_{PtC}$	490.7	--
C_3	110.8	109.9
$^3J_{PC}$	--	5.3
$^3J_{PC}$	9.5	10.0
$^2J_{PtC}$	0	0

[a] All spectra were recorded in $CDCl_3$.

[b] Chemical shifts are in ppm and coupling constants are in Hz.



127

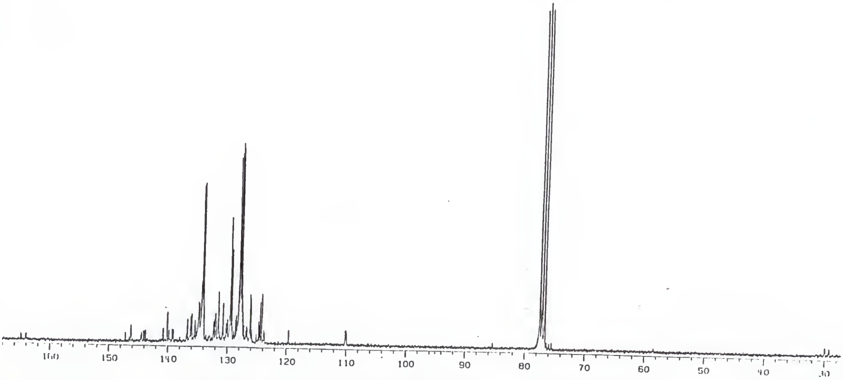
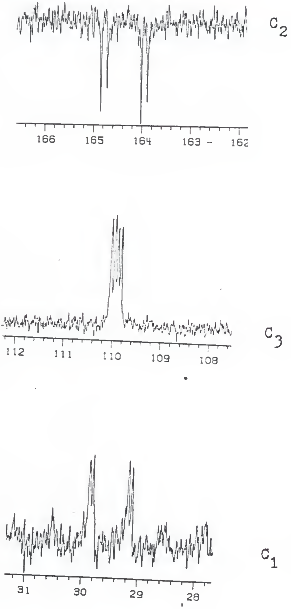
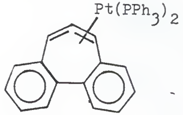


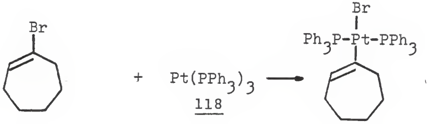
Figure 26. ^{13}C NMR spectrum (75MHz) of 127.





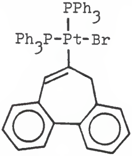
127

Figure 27. Expansions of ^{13}C NMR spectrum of 127 showing C$_1$-C$_3$.

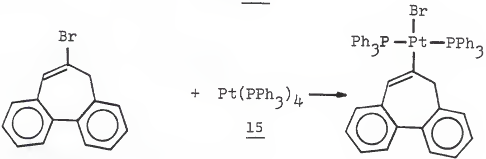


132 118 133

Since the cis insertion product, 134, would show an ABX pattern in its phosphorous NMR spectrum which might be similar to that of the allene complex, the thermal



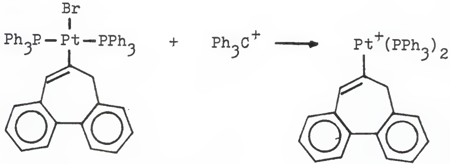
134



124 15 135

insertion reaction of 124 with 15 studied. The product of this reaction is the trans adduct, 135, as shown by the phosphorous NMR in which there are large platinum phosphorous coupling constants of 3189Hz and 3222Hz, which is a simple 1:4:1 triplet, with equivalent phosphorous atoms.

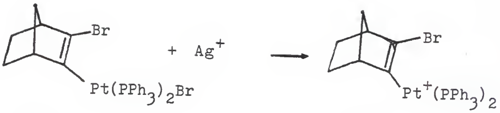
Hydride abstraction from sigma complexes has been useful in the synthesis of transition metal cycloheptatrienylidene complexes.[37-39] The reaction of insertion product 135 with trityl cation was studied in methylene chloride at -78°C. This gave an insoluble material assigned



135

136

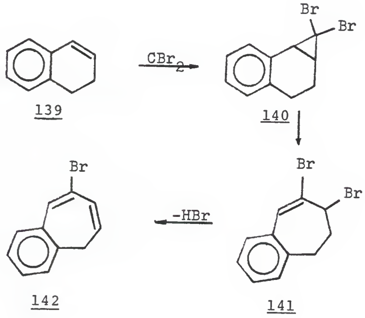
structure 136. A similar observation was made when 137 was treated with silver ion. Since no triphenylmethane was observed and therefore no hydride abstraction had occurred, no further work with this material was attempted.



137 138

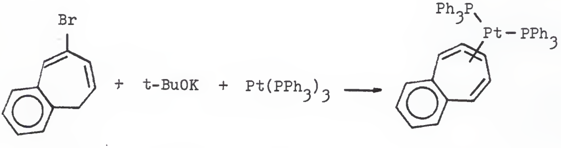
With the successful synthesis of the dibenzocycloheptatetraene complex, 127, the synthesis of the benzocycloheptatetraene complex was undertaken. This allene has been reported previously;[63] so it was only necessary to generate the intermediate in the presence of the tris(triphenylphosphine)platinum trap.

The bromoalkene precursor, 142, was prepared by the method of Waali et al., as outlined below.[63] Slow addition of



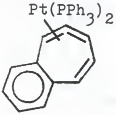
139 140 142 141

this to a THF solution of 118 and 126 gave the allene complex 143. The ^{1}H, ^{13}C, and ^{31}P -NMR spectra (cf Figure 28.) show that is the allene 143 and not the carbene complex. The NMR data for this compound are reported with that for the cycloheptatetraene complex, *vide infra*.

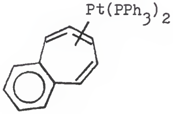


141 126 118 143

For allene complex 143 two regioisomers are possible. From steric considerations one expects the platinum to complex away from the benzannelation, as in 143. This is



144



143

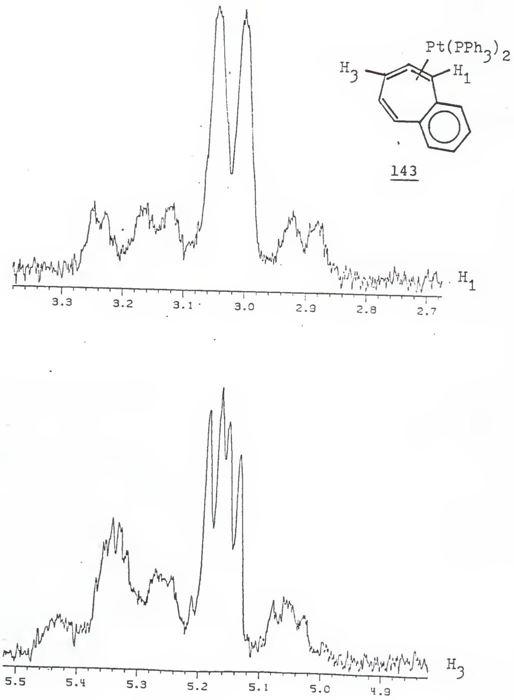
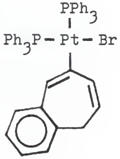


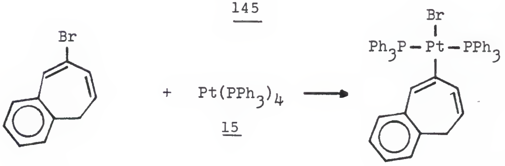
Figure 28. Expansions of ^{1}H NMR spectrum of 143 showing H$_1$ and H$_3$.

consistent with the chemical shifts and coupling constants of the allene hydrogen atoms. The dibenzocycloheptatetraene complex 127 and parent cycloheptatetraene complex were used as model systems. In complex 143 the coordinated hydrogen should be similar to the analagous hydrogen in the cycloheptatetraene complex, while in complex 144 the coordinated hydrogen should be as in the dibenzocycloheptatetraene complex. Similar logic can be used for the uncoordinated allene hydrogen, and both are consistent with the assignment of structure 143.

Again, there was the possibility of the formation of the cis-insertion product 145. The reaction of bromoalkene 142 with 15 in benzene was studied and the trans-insertion



145

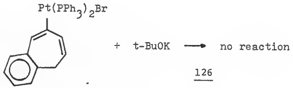


142

15

146

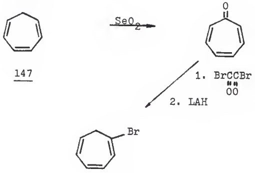
product was formed as shown by the triplet in the phosphorous spectrum. It was postulated that the insertion product might form during the reaction of bromoalkene 142 with base and 118 and that the insertion product reacted with base to give the allene. However, there was no reaction between the insertion product and base under the reaction conditions.



146

126

It remained to synthesize the parent cycloheptatetraene complex. Bromocycloheptatriene was prepared as a mixture

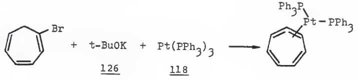


147

148

149

of three isomers according to the procedure of Fohlish and Haug.[64] Slow addition of one equivalent of bromocycloheptatriene to a solution of potassium tert-butoxide and tris(triphenylphosphine)platinum gave the cylcoheptatetraene complex 150, as characterized by ^{1}H, ^{13}C, and ^{31}P NMR (cf Figure 29,30). The spectroscopic data for the allene complex are summarized along with those for the benzocycloheptatetraene complex and the dibenzocycloheptatetraene complex in Tables 5-7.

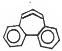


149

150

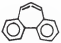
Cycloheptatetraene complex 110 was calculated by EHMO to be of comparable energy to cycloheptatrienylidene complex 111. In the carbene complex 151 H_a and H_b are equivalent and should have the same NMR shift. To probe the possibility of interconversion of the cycloheptatetraene complex with its valence isomer, variable temperature NMR studies were performed. On heating to 80°C there is no change in the ^{1}H-NMR spectrum, this is equivalent to a barrier separating the two valence isomers of at least 17 kcal/mol.[65]

Table 5. ^{13}C NMR data for 150, 143, and 127.[a,b]

			
	150	143	127
C_1	27.7	26.41	29.5
$^2J_{PC}$	5.1	4.9	5.4
$^2J_{PC}$	44.1	43.9	52.2
C_2	151.0	156.1	164.4
$^2J_{PC}$	10.4	9.7	9.6
$^2J_{PC}$	61.0	62.3	62.9
C_3	114.5	113.0	109.9
$^3J_{PC}$	9.3	--	10.0
$^3J_{PC}$	5.6	--	5.3

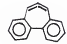
[a] All spectra were recorded in $CDCl_3$.
[b] Chemical shifts are in ppm and coupling constants are in Hz.

Table 6. ^{31}P NMR data for allene complexes 150, 143, and 127.[a,b]

	 150	 143	 127
P_1	31.5	30.5	29.0
$^2J_{PP}$	33.3	30.1	28.0
$^1J_{PtP}$	3267	3297	3208
P_2	27.3	26.2	27.5
$^1J_{PtP}$	3170	3131	3145

[a] All spectra were recorded in $CDCl_3$.
[b] Chemical shifts are in ppm and coupling constants are in Hz.

Table 7. ^{1}H NMR data for H_1 and H_3 of 150, 143, and 127.[a,b]

			
	150	143	127
H_1	2.94	3.02	3.48
$^2J_{PtH}$	70.4	72	70.8
$^3J_{PH}$	11	13.2	--
H_2	4.63	5.16	5.71
$^3J_{PtH}$	70.8	66	54.6
$^4J_{PH}$	9	9	8.35
$^4J_{PH}$	7	4.5	2.8
$^4J_{HH}$	--	--	2.8

[a] All spectra were recorded in $CDCl_3$ at 300MHz.
[b] Chemical shifts are reported in ppm and coupling constants are in Hz.

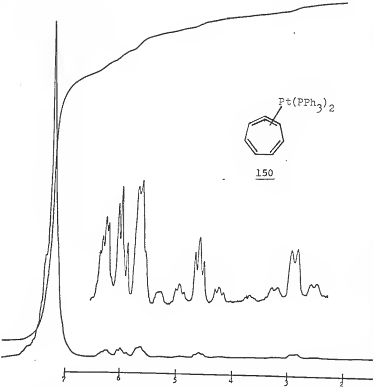
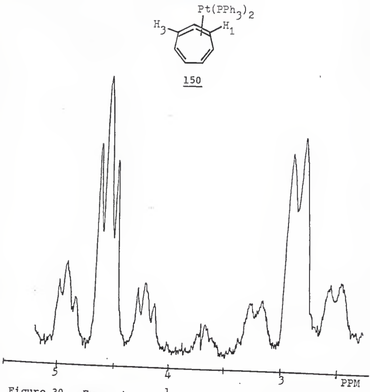
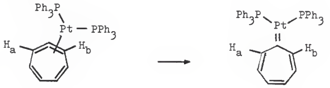


Figure 29. ^{1}H NMR spectrum (100MHz) of 150.



150

Figure 30. Expansion of ^1H NMR spectrum of 150 showing H_1 and H_3.



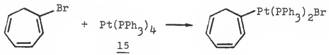
150 151

$$\Delta G^{\neq} = RT_c(\ln Tc/\delta\nu + 22.96) \quad \text{Eq (2)}$$

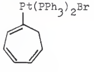
T_c = coalescence temperature

$\delta\nu$ = peak separation in Hz

The insertion reaction of bromocycloheptatriene with tetrakis(triphenylphosphine)platinum was studied. The trans-isomer was formed and when excess bromocycloheptatriene was used, the 1-isomer was the major product. This material was inert to potassium tert-butoxide in THF at room temperature.



149 152



152

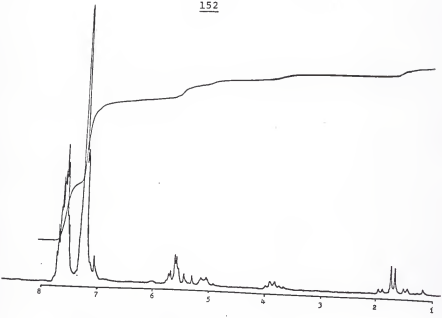
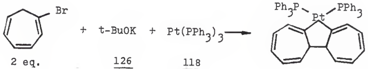


Figure 31. ^1H NMR spectrum (100MHz) of 152.

Initially there was difficulty in isolating the cycloheptatetraene complex and the reaction was attempted using two equivalents of bromocycloheptatriene and excess base. The product of the reaction was the novel bis-adduct 153 which has been characterized by ^{1}H, ^{13}C, ^{31}P-NMR (cf. Figures 32 to 36), comparison of these data with that for model compounds, and an x-ray crystal structure determination.

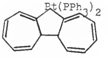


2 eq. 126 118

149

153

Integration of the ^{1}H-NMR, shown in Figure 32, shows there to be a 1:1 ratio of triphenylphosphine to cycloheptatetraene. Notice there is a high field proton, 1.68 ppm which is coupled to platinum.



153

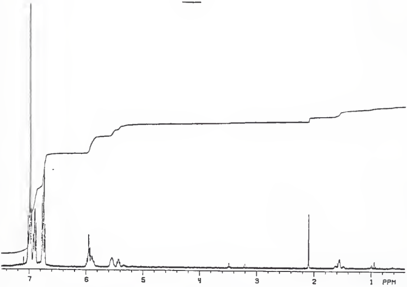
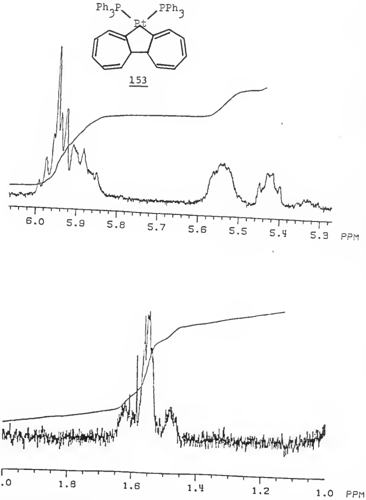


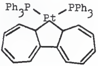
Figure 32. ^{1}H NMR spectrum (300MHz) of 153.



153

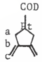
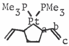
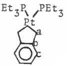
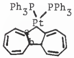
Figure 33. Expansion of ^{1}H NMR spectrum of 153 showing high field region.

Consideration of the ^{13}C-NMR spectrum, shown in Figure 34, and comparison with the ^{13}C NMR spectra of known platinacyclopentanes shows the compound to be a platinacyclopentane with the regiochemistry shown. Most important for the assignment is a resonance at 157.6 ppm with a small coupling constant of 8.5 Hz and a large coupling constant of 105.16 Hz, consistent with two bond cis- and trans- phosphorous coupling. One would expect to see a platinum coupling constant of about 900 Hz, unfortunately signal to noise limitations prevented observation of the peaks. However, the platinum coupling was observed in a derivative, vide infra. The phosphorous coupling constants show the carbon to be bonded to platinum and the chemical shift and multiplicity are consistent with a vinylic assignment. This eliminates 154 as a possible structure. At 57.8 ppm is a peak for carbon bonded to



154

Table 8. NMR data for some platinum metallacyclopentanes.[a]

				
	155	156	157	153
C_a	33.5	48.1	36.0	157.6
$^1J_{PtC}$	725	584	600	--
$^2J_{PC}$	na	7.3	9	8.5
$^2J_{PC}$	na	93	92	105.1
C_b	162	148.9	157.5	57.8
$^2J_{PtC}$	0	60	37	119
$^3J_{PC}$	na	0	4	0
C_c	101.2	102.7	132.7	na
$^3J_{PtC}$	82	55	86	na
$^4J_{PC}$	na	7.3	3	na
Ref.	66	66	67	

[a] Chemical shifts are reported in ppm and coupling constants are in Hz.

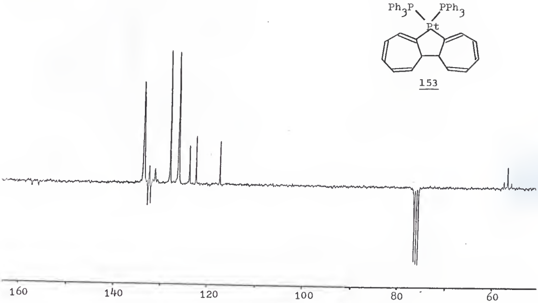
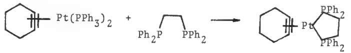


Figure 34. ^{13}C NMR spectrum (75MHz) of 153.

hydrogen and showing a platinum coupling constant of 119 Hz, both these facts are consistent with structure 153.

Finally, the phosphorous NMR spectrum, shown in Figure 35, yields a simple 1:4:1 triplet at 25.7 ppm with a platinum coupling constant of 1960.5 Hz. All the phosphorous nuclei must be equivalent. Table 9 shows some typical phosphorous shifts and coupling constants for known cis-platinum(II) phosphorous compounds. The similarity of the coupling constant for 153 with those of the compounds in Table 9 is consistent with the assignment of a cis-platinum(II) phosphorous compound.

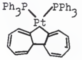
For further confirmation of the structure a derivative was synthesized. Bennet and Yoshida had reported that heating 119 with DIPHOS 161 led to exchange of the phosphorous ligands and formation of 162.[54]



119 161 162

DIPHOS

Table 9. ^{31}P NMR data for some cis-phosphorous platinum compounds.

Coumpound	Shift(ppm)	$^{1}J_{PtP}$(Hz)
$Pt(PEt_3)_2Me_2$ 158	-9.7	1856
$Pt(PEt_3)_2Ph_2$ 159	-3.5	1705
$Pt(PMe_2Ph)_2Me_2$ 160	11.2	1819
 153	25.7	1961

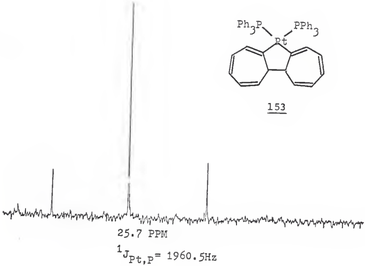
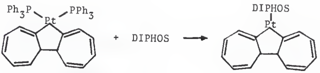


Figure 35. ^{31}P NMR spectrum (121MHz) of 153.

Heating 153 with excess DIPHOS also led to exchange. This compound was characterized by ^1H, ^{13}C, ^{31}P-NMR and elemental analysis and is similar to the parent in all respects. The one bond platinum carbon coupling constant was observed for 163, 904.7Hz.



153 161 163

Finally, the x-ray crystal structure proved the assignment for 153. The ortep drawing of 153 is in Figure 11. There was a large standard deviation in the determined C-C bond distances because the crystal was slightly deformed, the data was rapidly collected and the platinum and phosphorous atoms dominate the scattering pattern.

Once the structure was assigned, the generality of the bis-adduct formation was studied. An excess of benzocycloheptatetraene was reacted with tris(triphenylphosphine)-platinum and the bis-adduct 164 was isolated.

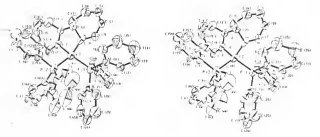


Figure 11. Stereo drawing of 153 produced by Ortep computer program.

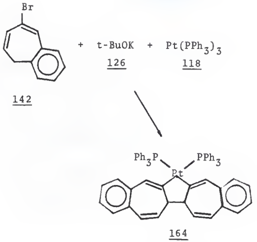
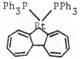
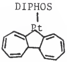
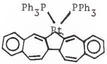
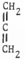


Table 10 summarizes the NMR data for 153, 163, and 164. These are the only compounds which have been observed to form the novel bis-adduct. For example, when an excess of the dibenzocycloheptatetraene 115 was generated in the presence of 116 only the allene complex 127 was formed, and in 70% yield. Similarly, no bis-adduct is formed when an excess of the saturated cyclic allene 51 is generated in the presence of the tris(triphenylphosphine)-platinum. Finally, no acyclic allenes have been reported to form bis-adducts with tris(triphenylphosphine)platinum.

Table 10. ^{31}P and ^{13}C NMR data for 153, 163, and 164.[a]

	 153	 163	 164
^{31}P	25.7	44.22	25.9
$^{1}J_{PtP}$	1960.5	1865.8	1950.8
C_7	57.8	58.1	57.3
$^{2}J_{PtC}$	119	114	98.6
C_1	157.6	161.8	168.6
$^{1}J_{PtC}$	--	904.7	--
$^{2}J_{PC}$	8.5	7.3	9.8
$^{2}J_{PC}$	105.1	108.4	103.8

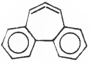
[a] All chemical shifts are reported in ppm and all coupling constants are in Hz.



$CH_2=C=CH_2$

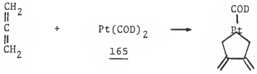
1

51



115

However, an excess of allene does react with "ligand free platinum", 165, to give the metallacyclopentane 155.[66]

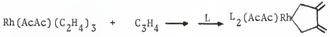


155

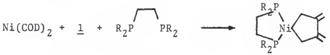
COD = 1,5-cyclooctadiene

Unfortunately, Barker et al.[66] did not study the reaction of 165 with any other allenes. While this is the only example of allene dimerization by platinum, numerous other metals are known to react with two equivalents of allene to form bis-adducts.[69,70]

For example,

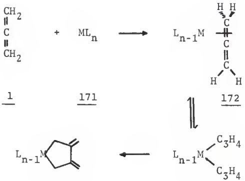


166 167



168 169 170

A mechanism which is consistent with all the above is outlined below. There is initial formation of the allene π-complex, and if there is only one equivalent of allene this is the major product. If there is excess allene

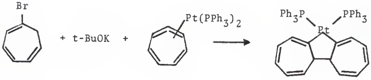


1 171 172

174 173

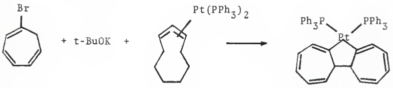
present, the mono allene adduct 172, can react with a second equivalent of allene to give a metal complex which has two allene ligands π-bonded, 173, This complex can either go on to the metallacyclopentane or lose one of the allenes. The transition state for metallacyclopentane formation is presumed to be very crowded. Thus, increasing substitution on the allene inhibits the metallacycle formation by steric blocking, as is observed in experiments.

Consistent with the proposed mechanism, reaction of cycloheptatetraene with 150 gives the metallocyclopentane 153.



149 150 153

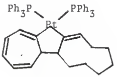
Interestingly, an attempt to make the unsymmetrical metallocyclopentane, 175, failed, reaction of cycloheptatetraene with 57 gave only 153. Apparently, loss of cyclononadiene to give 150 occurs more rapidly than metallocyclopentane formation.



149

57

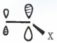
153

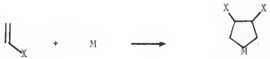


175

not formed

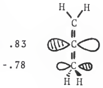
Metallacyclopentane formation from two allenes is a special case of metallacyclopentane formation from bis-olefin complexes. McKinney et al. have studied the formation of metallacyclopentanes from bis-olefin complexes and have also studied the affect of substituents on the regiochemistry of the reaction.[71] At the level of one electron theory the dominant interaction in this rearrangement is backbonding from the metal to the LUMO of the olefins. If the olefin is unsymmetrical the carbon-carbon bond formation should occur at the position which has the largest LUMO coefficient, as illustrated below.



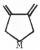


176

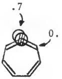
For 1,2-propadiene extended Huckel calculations show the largest coefficient in the LUMO to be at the central carbon, thus C-C bond formation should occur at the central carbon, leading to the observed regiochemistry. For cycloheptatetraene the largest coefficient is again at the central carbon, leading to the prediction of the same regiochemistry



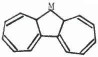
1



as is observed for 1,2-propadiene, which is not what is observed.



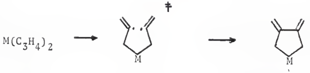
60



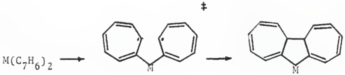
not
formed

177

Thus, the simple model proposed by McKinney et al.[71] is apparently not applicable to the allene reactions. Another explanation, which is consistent with the observed results is that there is much radical character in the transition state. For allene, a radical on the sp carbon is more stable than on the terminal sp^2 carbon and carbon bond formation occurs at the central carbon. For cycloheptatetraene the tropyl radical is more stable, leading to a reverse in the observed regiochemistry.



178 179 180



181 182 183

CHAPTER IV
SUMMARY

It has been reported that methoxy abstraction from 28 gives the allene complex 9, but that hydride abstraction from 64 gives the carbene complex 66. One objective of this research was a qualitative explanation for this result. EHMO calculations revealed that the Fp LUMO-ligand HOMO interaction is much greater with a sigma orbital than with a pi orbital. Thus, the relative energy of allene, 76, compared with planar allene, 77, decreases on complexation with Fp. But, the difference in energy of 76 and 77 is so great there is not any change in energy ordering. The energy difference between cycloheptatetraene, 93, and cycloheptatrienylidene, 94, is much smaller and on complexation with Fp there is a reversal in order.

Because no cycloheptatetraene transition metal complexes had been synthesized, a second objective of this research was the synthesis of a cycloheptatetraene transition metal complex. To this end, EHMO calculations were carried out which showed a significant difference in the bonding of Fp and $Pt(PPh_3)_2$ complexes, and which suggested the synthesis of a cycloheptatetraene bis(phosphine)platinum complex.

The generation of cycloheptatetraene in the presence of tris(triphenylphosphine)platinum led to rapid exchange and formation of a cycloheptatetraene transition metal complex. Similar reactions gave the benzocycloheptatetraene and dibenzocycloheptatetraene-bis(triphenylphosphine)-platinum complexes. These compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and by elemental analysis. These are the first examples of transition metal cycloheptatetraene complexes and demonstrate the significant difference in the bonding of Fp and $Pt(PPh_3)_2$.

A novel bis-adduct has been isolated from the reaction of excess cycloheptatetraene with tris(triphenylphosphine)platinum. While several transition metal complexes react with allene to form metallacyclopentanes, this is the first example of metallacycle formation with tris(triphenylphosphine)platinum. This bis-adduct, 153, has been characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and by an x-ray structure determination. The generality of this reaction was studied and benzocycloheptatetraene was the only other allene to show this novel reactivity.

CHAPTER V
EXPERIMENTAL

Benzene, diethyl ether, hexane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from P_2O_5 under nitrogen. Silica gel was M.C.B. 230-400 mesh. Alumina was Brockman 80-200 mesh, activity I, which was deactivated to activity II by the addition of 3% (w/w) water. ^1H and ^{13}C NMR were taken on a JEOL FX-100 (100MHz) or a Nicolet NC-300 (300MHz). ^{31}P NMR were recorded on a Nicolet NC-300 (121.4MHz) with trimethylphosphite used as an external reference. Elemental analysis were performed by University of Florida Microanalysis Service or by Atlantic Microlab, Inc. Melting points (uncorrected) were obtained using a Thomas Hoover apparatus. All solutions containing transition metals were manipulated under nitrogen either using a glove box or schlenk techniques.

Preparation of 7,7-dibromo-2,3-4,5-dibenzobicyclo[4.1.0]-heptane (122). This compound was prepared by the method of Allison.[55] Recrystallization from chloroform/hexane yielded white needles of 122: mp 131.0°-132.0°C; IR (nujol) 1580m, 780s cm^{-1}; ^{1}H NMR (100MHz, CDCl$_3$) 3.46(s,2H), 7.34(m,6H), 7.94(m,2H); ^{13}C NMR (25MHz, CDCl$_3$) 30.8(C7), 37.4(C1), 123.0, 128.1, 128.2, 129.5, 130.9, 131.2; Anal. Calcd. for $C_{15}H_{10}Br_2$: C,51.46; H,2.86. Found: C,51.37; H,2.68.

Preparation of 4,5-6,7-10,11-12,13-tetrabenzotricyclo[7.5.0.$0^{2,8}$]-tetradeca-2,3-4,5-6,7-10,11-12,13-14,11-hexaene(125). Potassium tert-butoxide (100mg, .9mmol) was weighed into a schlenk tube and 5 mL THF added. The bromoalkene[55], 124, (300mg,1.1mmol) was dissolved in 1 mL of THF and added to the solution in the schlenk tube. This solution was stirred overnight.

The reaction was quenched by filtering through alumina (neutral, grade II) and the solvent removed *in vacuo*. The resulting solid was purified by column chromatography. Elution on a 1" by 6" low pressure, silica gel column (230-400 mesh) with 7% methylene chloride/pentane and collection of the first band yielded 125 (92mg, 54%): mp. 153-155°C; ^{1}H NMR (100MHz, CDCl$_3$) δ4.42 (s,1H), 6.64(s,1H), 7.2-7.6(m, aromatic); ^{13}C NMR (25MHz, CDCl$_3$)δ47.2, 119.6, 124.5, 126.6, 127.8, 129.5, 131.8, 132.0, 135.8, 139.3, 139.9, 143.8, 147.1; mass spectrum, m/e 380 (parent ion); calcd for $C_{30}H_{20}$: 380.1557, found 380.1565.

Preparation of (1,2-η^2-4,5-6,7-dibenzocycloheptatetraene)-bis(triphenylphosphine)platinum (127). Potassium tert-butoxide (.35g, .31 mmol) and 118[72] (.75g, .76mmol) were weighed into an oven dried schlenk tube along with a magnetic stirrer. These were dissolved in 25 mL of THF, the schlenk tube was sealed with a septum, connected to a nitrogen line and cooled to 0°C.

Bromoalkene 124[55] (.5g, 1.43mmol) was weighed into a vial and transferred to a syringe with 1 mL of THF. This solution was added dropwise to the schlenk solution over fifteen minutes. After stirring overnight the solution was filtered through celite and the celite washed with THF. The solvent was removed *in vacuo* and the resulting oil triturated with 2 mL of ethanol. This was filtered and the precipitate washed with pentane. Drying *in vacuo* yielded 127 (.474g, 67%): mp. 144-150d; IR (KBr) 3050w, 2900w, 16602, 1585m, 1570w, 1475s, 1430s, 1180m, 1090s, 995m, 810m, 740s, 690s, 500s, 420m cm^{-1}; ^{1}H NMR (300MHz, CD_2Cl_2) δ3.48(t, $^{2}J_{PtH}$=70.8Hz), 5.71(tdt, $^{3}J_{PtH}$=54.6Hz, $^{4}J_{P(trans)H}$=8.35Hz, $^{4}J_{P(cis)H}$=$^{4}J_{HH}$=2.8Hz), 6.41(d,J=7.6Hz, 1H), 6.67(td, J=7.3Hz), 1.1Hz), 6.7-7.5(Ph_3P); ^{13}C NMR (75MHz, $CDCl_3$) δ29.5(dd, $^{2}J_{P(cis)C}$=5.43Hz, $^{2}J_{P(trans)C}$=52.2Hz, C5), 109.9(dd, $^{3}J_{PC}$=5.3Hz, $^{3}J_{PC}$=10Hz, C7), 124.11, 124.37, 125.96, 126.08, 130.68, 131.4, 134.66, 134.8, 140.03, 140.71(d,J=9.1Hz), 143.97(d,J=10.3Hz), 146.17, 164,36 (dd, $^{2}J_{P(cis)C}$=9.6Hz,

$^{2}J_{P(trans)C}$=62.9Hz,C2), 127.8(vt,$^{3}J_{PC}$=9.8Hz,Ph_3P, meta), 129.24(s,Ph_3P, para), 129.22(s, Ph_3P, para), 134.1(m, Ph_3P, meta), 135.385, 135.94, 136.10, 136.64(135-136, d, $^{1}J_{PC}$=2.5Hz, Ph_3P, ipso); ^{31}P NMR (121.5MHz, $CDCl_3$) δ28.97(td, $^{1}J_{PtP}$=3208Hz, $^{2}J_{PP}$=28Hz), 26.46(td, $^{1}J_{PtP}$=3145Hz, $^{2}J_{PP}$=28Hz); Anal. calcd for $C_{51}H_{40}P_2Pt_1$: C,67.33; H,4.75; Found: C,66.82; H,4.48.

Preparation of (1,2-η^2-1,2-cyclononadiene)bis-(triphenylphosphine)platinum (57). This compound was prepared according to the procedure of Visser and Ramakers[30]: mp 149-150°C; IR (KBr) 3060w, 2920w, 1590w, 1480m, 1440s, 1390m, 1180w, 1100s, 745m, 700s, 700s, 510s cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ1.0-2.3 (m,12H), 2.4(td,$^{2}J_{PtH}$=66Hz, $^{3}J_{PH}$=7Hz, H1), 4.95(td, $^{3}J_{PtH}$=74Hz, $^{4}J_{PH}$=10Hz, H3), 7.1-7.5(m, Ph_3P, 30H); ^{13}C NMR (75MHz, $CDCl_3$) δ22.84, 24.52, 26.20 (C5-C7), 29.80(d, J=11.0Hz), 31.64, 32.78(d, J=12.2Hz), 33.78(dd, $^{2}J_{P(trans)C}$=38.6Hz, $^{2}J_{P(cis)C}$=6.33Hz,1), 110.88(d, $^{3}J_{PC}$=9.5Hz, C3), 161.62(tdd, $^{1}J_{PtC}$=490.7Hz, $^{2}J_{P(trans)C}$=52.26Hz, $^{2}J_{P(cis)C}$=10.05Hz), 127.6(d, $^{3}J_{PC}$=9.5Hz, Ph_3P, meta), 128.85(s, Ph_3P, para), 133.9(m, Ph_3P, ortho), 136.75(t, $^{2}J_{PtC}$=22.9Hz, Ph_3P, ipso), 137.3(t, $^{2}J_{PtC}$=23.0Hz, Ph_3P, ipso).

Preparation of trans-(bromo)(η^1-cyclohepten-1-yl)bis(triphenylphosphine)platinum (133). Tetrabis(triphenylphosphine) platinum (200mg, .16mmol) and bromocycloheptene[73] (.05g, .28mmol) were weighed into a round bottom flask. A magnetic stirrer and 25 mL benzene were added and the solution refluxed under nitrogen for two hours.

The flask was cooled to room temperature and the solvent removed *in vacuo*. The solid was triturated with ether and filtered yielding 133 (116mg, 81%): mp 235-235.5d; IR (KBr) 3040w, 3020w, 1570m, 1500m, 1480s, 1430s, 1180m, 1090s, 740s, 690s, 520s cm^{-1}; ^1H NMR (100MHz, $CDCl_3$) δ.2-1.8(10H), 5.5 (H, $^3J_{PtH}$=74.7Hz, J_{HH}=5.37Hz,   Hz), 7.4(s, Ph_3P, 18H), 7.8(s, Ph_3Pm 12H); ^{13}C NMR (25MHz, $CDCl_3$) δ26.4, 26.8, 29.6, 32.5, 41.2, 139.9(Cl), 127.7(vt, $^3J_{PC}$=5.2, Ph_3P, meta), 129.9(s, Ph_3P, para), 131.9(vt, J=27.5Hz, Ph_3P, ipso), 135.4(m, Ph_3P, ortho); Anal. calcd. for $C_{43}H_{41}Br_1P_2Pt_1$: C,57.7; H,4.62; Found: C,57.42; H,4.66.

Preparation of trans-(bromo)(η^1-3,4-5,6-dibenzocycloheptatrien-1-yl)bis(triphenylphosphine)platinum (135).

Tetrahis(triphenylphosphine)platinum (350mg, .3mmol) was weighed into a round bottom flask equipped with a magnetic stirrer and nitrogen inlet bromoalkene 124 (180mg, .6mmol) in 25 mL toluene was added and the mixture heated overnight. In the course of the reaction there is a color change from bright orange to pale yellow.

The solvent was removed *in vacuo* and the solid triturated with hexane and filtered. The white precipitate was 135 (256mg, 86%): mp 281-283°d; IR (KBr) 3060w, 1590m, 1485s, 1440s, 1390s, 1195w, 1105s, 1000m, 840m, 755s, 695s, 520s cm^{-1};

^{1}H NMR (100MHz, CDCl$_3$) δ5.50(t, $^3J_{PtH}$=68.4Hz, 2H, H7), 6.6(m), 7.2(bs, Ph$_3$P); ^{13}C NMR (75MHz, CDCl$_3$) δ45.6(C7), 123.4(CH), 124.9(CH), 125.6(CH), 126.5(CH), 127.0(CH), 127.3(CH), 127.7 (Ph$_3$P, meta), 128.4, 129.1, 130.0 (Ph$_3$P, para), 132.1 (t, $^3J_{PC}$=7.2Hz, C2), 135.1 (vt, $^2J_{PC}$=6Hz, Ph$_3$P, ortho), 136.9, 139.2, 139.6, 139.8, 147.1 (t, $^2J_{PC}$=17.9Hz, C1); ^{31}P NMR (121.5MHz, CDCl$_3$) δ22.7 (t, $^1J_{PtP}$=3190Hz); Anal. calcd for $C_{51}H_{41}Br_1P_2Pt_1$: C,61.82; H,4.4; Found: C,62.93, H,4.25.
Preparation of (1,2-η^2-4,5-benzocycloheptatetraene)-bis(triphenylphosphine)platinum (143). Potassium tert-butoxide (57mg, .51mmol) and 118[72] (500mg, .51mmol) were weighed into an oven dried schlenk tube along with a magnetic stirrer. These were dissolved in 15 mL of THF, and the schlenk tube was sealed. The schlenk tube was connected to a nitrogen line and cooled to 0°C.

Bromoalkene 142[55] (113mg, .51mmol) was weighed into a vial and transferred to a syringe with 1 mL THF. This solution was added dropwise to the schlenk solution over fifteen minutes. After stirring overnight the solution was filtered through celite and the celite washed with 25mL ether. The solvent was removed *in vacuo* and the resulting oil triturated with 10mL hexane. This was filtered and the precipitate dried *in vacuo* yileding a white powder, 143 (360mg, 82%): mp 140-144d; IR: 3045w, 1480s, 1435s, 1385s, 1090s, 740s, 690s, 515s cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ3.02(td, $^2J_{PtH}$=72Hz, $^3J_{PH}$=13.2Hz, H1), 5.16(tdd, $^{3}J_{PtH}$=66Hz, $^{4}J_{PH}$=9Ha, $^{4}J_{PH}$=4.5Hz, H3), 6.07(d, J=12Hz), 6.13(d, J=12Hz), 6.32, 6.7(m), 7.0-7.7(m, Ph_3P); ^{13}C NMR (25MHz, $CDCl_3$) δ26.41(dd, $^{2}J_{P(trans)C}$=43.9Hz, $^{2}J_{P(cis)C}$=4.9Hz, C1), 113.0(mc, C2), 124.1, 125.8, 127.5 (bs_1, Ph_3P, meta), 128.6, 129.2(s, Ph_3P, para), 129.9, 130.4, 131.7, 132.1, 134.3(m, Ph_3P, ortho), 136.8 (Ph_3P, ipso, coupling not observed), 156.1(dd, $^{2}J_{P(trans)C}$=62.3Hz, $^{2}J_{P(cis)C}$=9.79Hz); ^{31}P NMR (121.4MHz, $CDCl_3$) δ26.2(td, $^{1}J_{PtP}$= 3134Hz, $^{2}J_{PP}$=30.1Hz), 32.2(td, $^{1}J_{PtP}$=3297Hz $^{2}J_{PP}$=30.1Hz); Anal. calcd for $C_{47}H_{38}P_2Pt_1$: C,65.67; H,4.46; Found: C,65.25; H,4.46.

Preparation of trans-(bromo)(4-η^1-1,2-benzocycloheptatriene-4-yl)bis(triphenylphosphine)platinum (146). Tetrakis(triphenylphosphine)platinum (1.0g, .8mmol) was weighed into a round bottom flask equipped with a magnetic stirrer and a nitrogen inlet. Bromoalkene, 142,[55] (200mg, .9mmol) in 25 mL benzene was added to this flask and the mixture refluxed 72 hours.

After cooling the flask to room temperature the solvent was removed *in vacuo* and the product triturated with ether. The precipitate was filtered and dried *in vacuo* to yield 146 (.46g, 61%): mp 218-219d; IR (KBr) 3065, 3020w, 1610w, 1485s, 1440s, 1390s, 1100s, 750m, 700s, 540s cm^{-1}; ^{1}H NMR (100MHz, $CDCl_3$) δ1.6(d, $^{3}J_{HH}$=3Hz, 47), 4.68(m, 1H), 5.8(td, $^{3}J_{PtH}$= 38Hz, J_{HH}=10Hz), 6.4-7.1(m, 5H), 7.2(18H, Ph_3P), 7.7(12H, Ph_3P); ^{13}C NMR (25MHz, CD_2Cl_2) δ33.3(C7), 121(t, $^{2}J_{PtC}$=72Hz), 124.7, 126.1, 126.2, 126.5, 128.1(d, ${}^3J_{PC}$=4.9Hz, Ph_3P, meta), 130.4, 130.5, (s, Ph_3P, para), 131.3(td, ${}^2J_{PtC}$=28Hz, ${}^1J_{PC}$=15.9Hz, Ph_3P, ipso), 134.4, 135.5(d, ${}^2J_{PC}$=6.1Hz, Ph_3P, ortho), 139.1, 142.8(d, ${}^2J_{PC}$=17.1Hz, C4); ${}^{31}P$ NMR (121.5MHz, $CDCl_3$) δ22.0(t, ${}^1J_{PtP}$=3189.4Hz); Anal. calcd for $H_{39}C_{47}Br_1P_2Pt_1$: C,60.0; H,4.18; Found: C,59.1, H,4.02.

Preparation of Tropone (148)

This compound was prepared by a modified procedure of Radlich from cycloheptatriene.[74] Instead of allowing the reaction mixture to stand overnight, it was stirred overnight with a mechanical stirrer in a Morton flask. This improved the yield to 37% (lit 25%).

Preparation of 1-,2-and 3-bromocycloheptatrienes (149). This isomeric mixture was prepared from bromotropylium bromide according to the method of Fohlisch and Haug.[75] A slight modification greatly simplified the work-up. Excess LAH was quenched with wet ether followed by addition of a saturated sodium potassium tartrate solution.[76]

Preparation of (1,2-η^2-cycloheptatetraene)bis(triphenylphosphine)-platinum (150). Potassium tert-butoxide (45mg, .401mmol) and tris(triphenylphosphine)platinum (400mg., .41mmol) were weighed into an oven dried schlenk tube and a magnetic stirrer added. After adding 10 mL of THF, the schlenk tube was sealed with a rubber septum, removed from the drybox, and connected to a nitrogen line.

Bromocycloheptatriene (69.4mg, .4mmol) was weighed into a vial and 1 mL of THF added. This solution was drawn into a syringe and added dropwise to the solution in the schlenk tube over ten minutes. After stirring overnight the solution was filtered through celite and the celite washed with 25 mL ether.

The solvent was removed *in vacuo* and this was triturated with 25 mL hexane. Filtration of this mixture yielded the light-yellow 150 as a powder (170mg, 51%): mp 140-144^{o}C d; IR (KBr) 3045w, 3000w, 1585m, 1570s, 1480s, 1430s, 1090s, 740s, 700s, 520s cm^{-1}; ^{1}H NMR (100MHz, $CDCl_3$) δ2.94(td, $^{2}J_{PtH}$=70.4Hz, $^{3}J_{PH}$=11Hz, H1), 4.63(tdd, $^{3}J_{PtH}$=70.8Hz, J=9Hz, J=7Hz), 5.64(m, 2H), 6.0(t, J=4Hz, 1H), 6.24(m, 1H), 7.2(Ph_3P, 30H); ^{13}C NMR (25MHz, $CDCl_3$) δ27.7(dd, $^{2}J_{P(cis)C}$=5.09Hz, $^{2}J_{P(trans)C}$=44.10Hz), 114.5(dd, $^{3}J_{PC}$=5.6Hz, $^{3}J_{PC}$=9.3Hz, C3), 118.5, 125.7, 127.7(d, J=8.6Hz, Ph_3P, meta), 129.2(s, Ph_3P, para), 133.5(m, Ph_3P, ortho), 136.0(vd, $^{1}J_{PC}$=41.7, Ph_3P, ipso), 151.0(dd, $^{2}J_{P(cis)C}$=10.4Hz, $^{2}J_{P(trans)C}$=60.98Hz, C2); ^{31}P NMR (121.5MHz, $CDCl_3$) δ27.3(td, $^{1}J_{ptP}$=3170.1Hz, $^{2}J_{PP}$=33.3Hz), 31.5(td, $^{1}J_{PtP}$=3266.7Hz, $^{2}J_{PP}$=33.3Hz); Anal. calcd for $C_{43}H_{36}P_2Pt_1$: C,63.74; H,4.45; Found: C,63.45; H,4.46.

Preparation of bromo(1-η^{1}-cycloheptatrienyl)bis(triphenylphosphine)platinum (152). Tetrahis(triphenylphosphine)platinum (1.07g, .86mmol) was weighed into a round bottom flask equipped with a magnetic stirrer and a nitrogen inlet. Bromocycloheptatriene (1.0g, 5.85mmol) in 50 mL benzene was added and the mixture stirred overnight.

The solution was removed in vacuo and the product triturated with 50 mL of ether. The precipitate was filtered and dried in vacuo to give 152 (.680g, 89%): mp 216.0-216.5 d; IR (KBr) 3050w, 3010w, 1571w, 1505m, 1480m, 1430s, 1385m, 1180m, 1100s, 1030m, 1000m, 750m, 700s, 500s cm^{-1}; ^{1}H NMR (100MHz, CDCl$_3$) δ2.23(td, $^3J_{PtH}$=39Hz, J_{HH}=7.1Hz, H7), 4.30(dt, J=6.84Hz, J=6.0Hz, 1H), 5.6(t, J_{PtH}=32Hz, 1H), 5.64(s, 2H), 6.0(s, 3H), 7.2(Ph$_3$P, 18H), 7.7 (Ph$_3$P, 12H); ^{13}C NMR (75MHz, CDCl$_3$) δ80.5(C7), 115.4, 122.9, 124.58, 127.70 (t, $^3J_{PC}$=5.27Hz, Ph$_3$P, meta), 130.1(s, Ph$_s$P, para), 131.0 (t, $^2J_{PtC}$=46Hz, Ph$_3$P, ipso), 14.3, 134.45, 135.2(m, Ph$_3$P, ortho), 139.4(C1); ^{31}P NMR (121.5MHz, CDCl$_3$) δ21.34(t, $^1J_{HP}$=3215Hz); Anal. calcd for $C_{43}H_{37}Br_1P_2Pt_1$: C,57.94; H,4.15; Found: C,57.76, H,4.23.

Preparation of (7'7-cycloheptatrienyl-7-cycloheptatriene-1,1'-diyl)bis(triphenylphosphine)platinum (153).

Tris(triphenylphosphine)platinum (1.75g, 1.78mmol) and potassium tert-butoxide (.60g, 5.33mmol) were weighed into a dry schlenk tube equipped with a magnetic stirrer. This was dissolved in 15 mL of THF and a septum used to seal the schlenk tube. After removing from the dry box this was connected to a nitrogen line and cooled to 0°C.

Bromocycloheptatriene (910mg, 5.33mmol) was weighed in a dry vial and then .5 mL of THF added. This solution was drawn into a syringe and added dropwise over ten minutes to the solution in the schlenk tube. The mixture was stirred overnight.

The brown solution was filtered through celite and the solvent removed from the filtrate in vacuo. Trituration of this solid overnight with hexane yields pure 153 (1.48g, 93%): mp 154-5°C d; IR (KBr) 3050w, 3010w, 1480m, 1440s, 1390m, 110-m, 740m, 700s, 520s cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$) δ1.68(t, $^3J_{PtH}$=43.5Hz, H7, H7^1), 5.65(t, J_{PtH}=58.5Hz, 2H), 5.75(m, 2H), 6.15(m, 6H), 6.66-7.4(m, 30H, Ph_3P); ^{13}C NMR (75MHz, $CDCl_3$) δ57.76(t, $^2J_{PtC}$=118.95, C7), 118.54, 123.64, 125.06, (C_3-C_5), 127.44(vt, $^3J_{PC}$=4.4Hz, Ph_3P, meta), 129.23 (s, Ph_3P, para), 132.39(t, $^2J_{PtC}$=75Hz, C_2), 133.58(vd, $^1J_{PC}$=45Hz, Ph_3P, ipso), 133.62(C_6), 134.79(vt, $^2J_{PC}$=5.7Hz, Ph_3P, ortho), 157.62(dd, $^2J_{P(cis)C}$=8.5Hz, $^2J_{P(trans)C}$=105.12Hz, Cl); ^{31}P NMR (41MHz, $CDCl_3$) δ25.7(t, $^1J_{PtH}$=1960.5Hz).

Preparation of (7'-cycloheptatrienyl-7-cycloheptatriene-1,1'-diyl)(1,2-bisdiphenylphosphinoethane)platinum (163). The bisadduct, 153, (510mg, .57mmol) was weighed into a round bottom flask and toluene added. Diphos, 161, 250mg, .63mmol) was added to the flask along with a reflux condenser and the solution refluxed overnight.

After cooling, the solution was concentrated to 15 mL and 20 mL of hexanes added. This was concentrated to 15 mL and filtered, yielding orange 163 (270mg, 61%): mp 170-75°C d; IR (KBr): 3040w, 3000w, 1575w, 1482m, 1435s, 1385m, 1188m, 1100m, 690s, 725m, 740m, 530m; ^{1}H NMR (100MHz, C_7D_8) δ1.4-2.0(m, 4H, diphos), 2.52(t, $^3J_{PtH}$=34Hz), 6.2-6.8(m, C_7H_6), 7.0(s, Ph_3P), 7.4-7.8m (Ph_3P); ^{13}C NMR (75MHz, $CDCl_3$)

δ30.21-30.95(m, diphos), 58.07(t, $^{2}J_{PtC}$=114.2Hz, C_7), 119.45, 123.39, 126.08, 128.14(d, $^{3}J_{PC}$=5.1Hz, diphos, meta), 128.21(d, $^{3}J_{PC}$+4.7Hz, diphos, meta), 128.657(d, $^{3}J_{PC}$=4.8Hz, diphos, meta), 128.72(d, $^{3}J_{PC}$=5.0Hz, diphos, meta), 130.4(s, diphos, para), 130.59(s, diphos, para), 131.79(diphos, ipso), 132.75(diphos, ipso), 153.45-134.26(m, diphos, ortho), 161.76(tdd, $^{1}J_{PtC}$=904.8Hz, $^{2}J_{P(cis)C}$=7.29Hz, $^{2}J_{P(trans)C}$= 108.38Hz); ^{31}P NMR (121.4MHz, $CDCl_3$) δ44.2(t, $^{1}J_{PtP}$=1865.8Hz); Anal. calcd for $C_{40}H_{36}P_2Pt_1$: C,61.95, H4.68; Found: C,63.29; H,5.09.

Preparation of (7'-3',4'-benzocycloheptatrienyl-7-3,4-benzocycloheptatrien-1,1'-diyl)bis(triphenylphosphine)-platinum (164). Tris(triphenylphosphine)platinum (500mg, .51mmol) and potassium tert-butoxide (150mg, 1.34mmol) were weighed into a dry schlenk tube equipped with a magnetic stirrer. These were dissolved in 5 mL of THF and the schlenk tube sealed with a septum. The schlenk tube was connected to a nitrogen line and cooled to 0^{o}C.

Bromoalkene 142 (250mg, 1.14mmol) was weighed into a dry vial and then .5 mL of THF added. This solution was drawn into a syringe, removed from the dry box and added dropwise over ten minutes to the solution in the schlenk tube. After adding the solution from the syringe, the mixture was allowed to stir overnight.

The resulting brown solution was filtered through celite and the celite washed with 25 mL ether. The solvent was removed in vacuo and the product triturated with hexane overnight. Filtration yielded the off white powder, 164. (.22mmol, 44%): mp 140-146°C d; IR (KBr) 3050w, 3000w, 1585m, 1475s, 1435s, 1383w, 1310w, 1180w, 1090m, 1000m, 840w, 740s, 690s cm^{-1}; ^1H NMR (100MHz, $CDCl_3$) δ3.38(t, $^3J_{PtH}$=28Hz, H7), 5.4-6.4(m, 6H), 7.2-7.7(m, Ph_3P, 38H); ^{13}C NMR (25MHz, $CDCl_3$) δ57.3(t, $^2J_{PtC}$=98.6), 123.15, 123.6, 124.6, 125.1, 125.9, 127.6(d, $^3J_{PC}$=5.2Hz, Ph_3P, meta), 129.4(s, Ph_3P, para), 129.8, 130.0, 131.9, 132.6(Ph_3P, ipso); 134.9(m, Ph_3P, ortho), 137.6, 140.0, 168.6(dd, $^2J_{P(cis)C}$=9.8Hz, $^2J_{P(trans)C}$=103.8Hz); ^{31}P NMR (121.4MHz, $CDCl_3$) δ25.9 ($^1J_{PtP}$=1950,8Hz).

Reaction of 135 with potassium tert-butoxide.

Potassium tert-butoxide (43mg, .38mmol) and insertion product 135 (53mg, 50mmol) were weighed into a round bottom flask and 20 mL THF added. The mixture was stirred overnight and then filtered through celite. The solvent was removed in vacuo and the product triturated with ethanol, yielding 135 (39mg, 39mmol).

Similar experiments were performed with the insertion products 146 and 152 with like results.

The reaction of heptafulvalene with potassium tert-butoxide and tris(triphenylphosphine)platinum. Heptafulvalene (53mg, .29mmol), potassium tert-butoxide (100mg, .89mmol), and tris(triphenylphosphine)platinum were weighed into a schlenk tube and 15 mL THF added. The schlenk tube was sealed with a septum and the mixture stirred overnight under nitrogen. After this it was filtered through alumina (20g, neutral, activity I, 80-200 mesh) and the alumina washed in vacuo. ^{1}H NMR of the crude mixture showed heptafulvalene and tris(triphenylphosphine)platinum identical with the starting material.

APPENDIX
EXTENDED HÜCKEL CALCULATIONS

All calculations were performed using the extended Hückel method. The Hii's are taken from the literature along with the orbital exponents used. The values for the Hii's and orbital exponents are listed in Table 11. The modified Wolfsberg-Helmholz formula was used in all calculations. The geometry for the Fp fragment is idealized and taken from the literature. The structure for bis(phosphine)platinum is based on the known structure of (ethylene)bis(triphenylphosphine)platinum. All organic structures were optimized using MINDO/3. Metal ligand distances were fixed at 2.0 Å.

Table 11. Parameters used in extended Huckel calculations.

Orbital	Hii,eV	δ_1	δ_2	C_1	C_2
Fe 3d	-12.70	5.35	1.8	0.5366	0.6678
4s	-9.17	1.90			
4p	-5.37	1.90			
Pt 5d	-12.59	6.01	2.70	0.6334	0.5513
6s	-9.08	2.55			
6p	-5.48	2.55			
P 3s	-18.60	1.60			
3p	-14.00	1.60			
C 2s	-21.40	1.625			
2p	-11.40	1.625			
H 1s	-13.60	1.30			

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Allene, 1

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	C
2	1	1.306	0	0.00	0	0.00	0	C
3	2	1.306	1	180.00	0	0.00	0	C
4	1	1.080	2	124.10	3	0.00	0	H
5	3	1.080	2	124.10	4	90.00	0	H

Planar allene, 77

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	C
2	1	1.343	0	0.00	0	0.00	0	C
3	1	1.343	2	124.24	0	0.00	0	C
4	2	1.080	1	131.25	3	0.00	0	H
5	2	1.080	1	123.27	3	180.00	0	H
6	3	1.080	1	131.25	2	180.00	0	H
7	3	1.080	1	123.27	2	0.00	0	H

Cyclopropylidene, 78

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	C
2	1	1.484	0	0.00	0	0.00	0	C
3	1	1.484	2	60.08	0	0.00	0	C
4	2	1.080	1	120.37	3	110.13	0	H
5	3	1.080	1	120.37	2	110.13	0	H

Cycloheptatetraene, 93

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	2.450	0	0.00	0	0.00	0	C
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	1.323	2	74.70	0	90.00	0	C
4	3	1.470	1	113.40	2	23.98	0	C
5	4	1.366	3	122.30	1	-36.03	0	C
6	1	1.323	3	149.40	4	23.98	0	C
7	6	1.470	1	113.40	3	23.98	0	C
8	7	1.366	6	122.30	1	-36.03	0	C
9	3	1.090	1	126.20	6	210.08	0	H
10	6	1.090	1	126.20	3	210.08	0	H
11	4	1.090	3	117.40	1	146.87	0	H
12	7	1.090	6	117.40	1	146.87	0	H
13	5	1.090	4	117.60	3	184.25	0	H
14	8	1.090	7	117.60	6	184.25	0	H

Cycloheptatrienylidene, 94

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	C
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	1.386	2	67.25	0	0.00	0	C
4	3	1.392	1	125.90	2	0.00	0	C
5	4	1.420	3	127.30	1	0.00	0	C
6	3	1.090	1	117.10	2	180.00	0	H
7	4	1.090	3	117.50	6	0.00	0	H
8	5	1.090	4	114.70	7	0.00	0	H
9	1	1.390	3	134.50	4	0.00	0	C
10	9	1.390	1	125.90	2	0.00	0	C
11	10	1.420	9	127.30	1	0.00	0	C
12	9	1.090	1	117.10	2	180.00	0	H
13	10	1.090	9	117.50	12	0.00	0	H
14	11	1.090	10	114.70	13	0.00	0	H

Bicyclo[4.1.0]hepta-2,4-dien-7-ylidene, 95

Atom	X	y	z
H	-0.52	0.87	1.91
H	1.92	0.87	0.55
H	-1.29	-1.17	2.85
H	3.11	-1.22	0.39
H	0.12	-3.25	2.80
H	2.28	-3.28	1.57
C	1.66	-2.37	1.49
C	0.02	0.30	-0.01
C	-0.14	-0.05	1.39
C	1.29	-0.05	0.60
C	-0.39	-1.24	2.21
C	2.09	-1.26	0.82
C	0.39	-2.35	2.21

1,2-cyclohexadiene, 84

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	C
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	1.339	2	68.42	0	0.00	0	C
4	3	1.507	1	112.54	2	0.00	0	C
5	4	1.540	3	112.36	1	-29.06	0	C
6	1	1.339	3	136.84	4	16.00	0	C
7	6	1.510	1	112.54	3	16.00	0	C
8	3	1.090	1	127.06	6	-153.02	0	H
9	4	1.090	3	105.73	1	-145.23	0	H
10	4	1.090	3	117.95	1	99.78	0	H
11	5	1.090	4	107.54	7	107.54	-1	H
12	5	1.090	4	107.27	7	107.27	1	H
13	6	1.090	1	127.06	3	-153.02	0	H
14	7	1.090	6	105.73	1	-145.23	0	H
15	7	1.090	6	117.95	1	99.78	0	H

Planar-1,2-cyclohexadiene, 85

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	C
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	1.378	2	56.50	0	0.00	0	C
4	3	1.506	1	128.15	2	0.00	0	C
5	4	1.520	3	115.13	1	-17.86	0	C
6	1	1.378	3	113.03	4	5.10	0	C
7	6	1.506	1	128.15	3	5.10	0	C
8	3	1.090	1	119.20	6	-175.72	0	H
9	4	1.090	3	111.34	1	-147.80	0	H
10	4	1.090	3	104.32	1	101.66	0	H
11	5	1.090	4	109.00	7	109.00	1	H
12	5	1.090	4	109.00	7	109.00	-1	H
13	6	1.090	1	119.20	3	-175.72	0	H
14	7	1.090	6	111.34	1	147.80	0	H
15	7	1.090	6	104.32	1	-101.66	0	H

Bicyclo[3.1.0]hexan-6-ylidene, 86

Atom	X	Y	Z
H	1.55	-0.75	3.55
H	-1.55	-0.75	3.55
H	00.0	1.80	5.48
H	0.0	3.13	4.40
H	-2.10	1.34	4.42
H	1.61	2.04	2.91
H	-1.61	2.04	2.91
H	2.10	1.34	4.42
C	0.0	2.02	4.38
C	0.88	0.05	3.14
C	-0.88	0.05	3.14
C	1.23	1.39	3.73
C	0.0	-0.59	2.24
C	-1.23	1.39	3.73

(η^2-allene)dicarbonylcyclopentadienyliron, 72

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	XX
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	4	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

$(\eta^2$-allene)dicarobnylcyclopentadienyliron, 72-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	2	0.717	1	90.00	3	90.00	0	C
19	2	0.717	1	90.00	3	-90.00	0	C
20	19	1.318	1	138.87	18	180.00	0	C
21	18	1.080	1	115.60	19	115.92	0	H
22	18	1.080	1	115.61	19	-115.92	0	H
23	20	1.080	19	121.32	1	180.00	0	H
24	20	1.080	19	126.37	1	0.00	0	H

(2-η^1-planar-allene)dicarbonylcyclopentadienyliron, 73

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	C
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	4	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

(2-η^1-planar-allene)dicarbonylcyclopentadienyliron, 73-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	2	1.410	1	124.96	3	90.00	0	C
19	2	1.410	1	124.96	3	-90.00	0	C
20	18	1.080	2	126.19	1	180.00	0	H
21	18	1.080	2	125.34	1	0.00	0	H
22	19	1.080	2	126.19	1	180.00	0	H
23	19	1.090	2	125.34	1	0.00	0	H

dicarbonylcyclopentadienyl(η^1-cyclopropylidene)iron

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABDC	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	XX
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	4	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

dicarbonylcyclopentadienyl(η^1-cyclopropylidene)iron-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	1	0.000	2	0.00	3	0.00	0	XX
19	2	0.000	1	0.00	3	0.00	0	C
20	19	1.480	18	148.99	3	0.00	0	C
21	19	1.480	18	148.99	20	180.00	0	C
22	20	1.080	19	121.68	18	72.15	0	H
23	20	1.080	19	121.68	18	-72.15	0	H
24	21	1.080	19	121.68	18	72.15	0	H
25	21	1.080	19	121.68	18	-72.15	0	H

dicarbonyl(η^2-1,2-cyclohexadiene)cyclopentadienyl iron, 91

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	XX
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	4	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

dicarbonyl(η^2-1,2-cyclohexadiene)cyclopentadienyl iron, 91-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	2	0.731	1	90.00	3	90.00	0	C
19	2	0.731	18	180.00	1	0.00	0	C
20	19	1.512	18	111.04	1	-120.31	0	C
21	20	1.539	19	113.35	18	-34.12	0	C
22	21	1.538	20	120.87	19	18.54	0	C
23	22	1.502	21	115.81	20	12.16	0	C
24	19	1.080	18	125.82	23	-123.94	0	H
25	23	1.080	18	124.69	19	-164.11	0	H
26	20	1.080	19	109.15	18	-155.59	0	H
27	20	1.080	19	111.86	18	91.25	0	H
28	22	1.080	21	109.07	20	-117.03	0	H
29	22	1.080	21	109.54	20	133.21	0	H
30	21	1.080	20	107.80	19	-105.91	0	H
31	21	1.080	20	108.12	19	144.51	0	H

dicarbonyl(2-η^1-planar-cyclohexadiene)cyclopentadienyl iron, 90

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	XX
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	3	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

dicarbonyl(2-η^1-planar-cyclohexadiene)cyclopentadienyl iron, 90-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	1	0.000	2	0.00	3	0.00	0	XX
19	2	0.000	1	0.00	3	0.00	0	C
20	19	1.435	1	125.20	3	0.00	0	C
21	20	1.481	19	128.92	1	176.08	0	C
22	21	1.519	20	116.58	19	-17.80	0	C
23	19	1.435	20	108.59	21	-4.03	0	C
24	23	1.481	19	128.92	18	-176.08	0	C
25	20	1.080	19	118.01	18	0.92	0	H
26	23	1.080	19	118.01	18	0.92	0	H
27	21	1.080	20	111.08	19	-147.32	0	H
28	21	1.080	20	105.72	19	102.79	0	H
29	24	1.080	23	111.08	19	147.32	0	H
30	24	1.080	23	105.72	19	-102.79	0	H
31	22	1.080	21	109.66	24	110.89	-1	H
32	22	1.080	21	110.32	24	109.52	1	H

(6-η^1-bicyclo[3.1.0]hexan-6-ylidene)dicarbonylcyclopentadienyl iron, 92

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	XX
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	4	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

(6-η^1-bicyclo[3.1.0]hexan-6-ylidene)dicarbonylcyclopentadienyl iron, 92-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	1	0.000	2	0.00	3	0.00	0	XX
19	1	2.000	2	0.00	3	0.00	0	C
20	19	1.490	1	146.74	3	0.00	0	C
21	20	1.528	19	119.15	1	-69.90	0	C
22	21	1.532	20	106.22	19	-81.16	0	C
23	19	1.490	20	63.81	21	91.73	0	C
24	23	1.528	19	119.15	20	-91.73	0	C
25	20	1.080	19	121.14	18	95.51	0	H
26	23	1.080	19	121.14	18	-95.51	0	H
27	21	1.080	20	114.68	19	149.63	0	H
28	21	1.080	20	107.88	19	31.33	0	H
29	24	1.080	23	114.68	19	-149.63	0	H
30	24	1.080	23	107.88	19	-31.33	0	H
31	22	1.080	21	111.42	20	-89.77	0	H
32	22	1.080	21	113.35	20	155.18	0	H

dicarbonyl(η^2-cycloheptatetranene)cyclopentadienyl iron, 99

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	XX
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	4	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

dicarbonyl(η^2-cycloheptatetranene)cyclopentadienyl iron, 99-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	2	0.000	1	0.00	3	0.00	0	XX
19	18	0.730	1	90.00	3	90.00	0	C
20	18	0.730	19	180.00	1	0.00	0	C
21	20	1.342	19	142.59	1	145.65	0	C
22	21	1.468	20	116.88	19	16.42	0	C
23	22	1.360	21	125.39	20	-31.75	0	C
24	23	1.468	22	128.64	21	1.22	0	C
25	24	1.350	23	130.30	22	24.27	0	C
26	19	1.080	20	125.77	21	-121.42	0	H
27	21	1.080	22	119.20	23	138.49	0	H
28	22	1.080	23	118.89	24	179.47	0	H
29	23	1.080	24	113.71	25	-155.22	0	H
30	24	1.080	25	117.44	19	176.16	0	H
31	25	1.080	19	117.78	20	144.21	0	H

dicarbonyl(η^1-cycloheptatrienylidene)cyclopentadienyl iron, 100

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	XX
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	4	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

dicarbonyl(η^1-cycloheptatrienylidene)cyclopentadienyl iron, 100-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	1	2.000	2	0.00	3	0.00	0	C
19	18	1.488	1	119.45	3	90.00	0	C
20	19	1.356	18	131.43	1	180.00	0	C
21	20	1.453	19	129.91	18	0.00	0	C
22	18	1.488	19	121.07	20	0.00	0	C
23	22	1.356	18	131.43	19	0.00	0	C
24	23	1.453	22	129.91	18	0.00	0	C
25	19	1.080	18	113.02	22	180.00	0	H
26	20	1.080	19	117.22	18	180.00	0	H
27	21	1.080	20	114.72	19	180.00	0	H
28	22	1.080	18	113.02	19	180.00	0	H
29	23	1.080	22	117.22	18	180.00	0	H
30	24	1.080	23	114.72	22	180.00	0	H

(η^1-bicyclo[4.1.0]hepta-2,4-dien-7-ylidene)dicarbonylcyclopentadienyl iron, 101

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	FE
2	1	2.000	0	0.00	0	0.00	0	XX
3	1	1.700	2	120.00	0	0.00	0	XX
4	3	1.216	1	90.00	2	36.00	0	C
5	4	1.430	3	54.00	1	90.00	0	C
6	5	1.430	4	108.00	3	0.00	0	C
7	6	1.430	5	108.00	4	0.00	0	C
8	7	1.430	6	108.00	5	0.00	0	C
9	4	1.090	8	126.00	3	180.00	0	H
10	5	1.090	4	126.00	9	0.00	0	H
11	6	1.090	5	126.00	10	0.00	0	H
12	7	1.090	6	126.00	11	0.00	0	H
13	8	1.090	7	126.00	12	0.00	0	H
14	1	1.750	3	127.60	2	90.00	1	C
15	14	1.130	1	180.00	2	0.00	0	O

(η^1-bicyclo[4.1.0]hepta-2,4-dien-7-ylidene)dicarbonylcyclopentadienyl iron, 101-continued

16	1	1.750	3	127.60	2	90.00	-1	C
17	16	1.130	1	180.00	2	0.00	0	O
18	1	2.000	2	0.00	3	0.00	0	C
19	18	1.485	1	147.72	3	0.00	0	C
20	19	1.488	18	124.80	1	76.71	0	C
21	20	1.357	19	122.67	18	61.79	0	C
22	18	1.486	1	147.72	3	180.00	0	C
23	22	1.486	18	124.80	1	-76.71	0	C
24	23	1.355	22	122.67	18	-61.79	0	C
25	19	1.080	20	113.78	21	-143.95	0	H
26	22	1.080	23	113.78	24	143.95	0	H
27	20	1.080	21	121.68	24	-172.30	0	H
28	23	1.080	24	121.68	21	172.30	0	H
29	21	1.080	20	122.08	27	-5.83	0	H
30	24	1.080	23	122.08	28	5.83	0	H

$(\eta^2$-allene)bisphosphine platinum, 103

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	2.000	2	180.00	3	0.00	0	XX
12	11	0.720	1	90.00	3	0.00	0	C
13	11	0.720	1	90.00	3	180.00	0	C
14	13	1.320	1	138.87	12	180.00	0	C
15	12	1.080	1	115.60	13	115.92	0	H

(η^2-allene)bisphosphine platinum, 103-continued

16	12	1.080	1	115.61	13	-115.92	0	H
17	14	1.080	13	121.32	10	180.00	0	H
18	14	1.080	13	126.37	10	0.00	0	H

(2-η^1-planarallene)bisphosphine platinum, 104

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	0.000	2	0.00	3	0.00	0	XX
12	11	2.000	2	180.00	3	0.00	0	C
13	12	1.410	11	124.96	3	90.00	0	C
14	12	1.410	11	124.96	13	180.00	0	C
15	13	1.080	12	126.19	11	180.00	0	H

(2-η^1-planarallene)bisphosphine platinum. 104-continued

16	13	1.080	12	125.34	11	0.00	0	H
17	14	1.080	12	126.19	11	180.00	0	H
18	14	1.080	12	125.34	11	0.00	0	H

(η^1-cyclopropylidene)bisphosphine platinum, 105

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	0.000	2	0.00	3	0.00	0	XX
12	1	2.000	2	180.00	3	0.00	0	C
13	12	1.480	1	148.99	3	90.00	0	C
14	12	1.477	11	148.99	13	180.00	0	C
15	13	1.080	12	121.68	11	72.15	0	H

(η^1-cyclopropylidene)bisphosphine platinum, 105-continued

16	13	1.080	12	121.68	11	-72.15	0	H
17	14	1.080	12	121.68	11	72.15	0	H
18	14	1.080	12	121.68	11	-72.15	0	H

(η^2-1,2-cyclohexadiene)bisphosphine platinum, 107

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	2.000	2	180.00	3	0.00	0	XX
12	11	0.731	1	90.00	3	0.00	0	C
13	11	0.731	12	180.00	3	0.00	0	C
14	13	1.512	12	111.04	1	-120.31	0	C
15	14	1.539	13	113.35	12	-34.12	0	C

(η^2-1,2-cyclohexadiene)bisphosphine platinum, 107-continued

16	15	1.538	14	120.87	13	18.54	0	C
17	16	1.502	15	115.81	14	12.16	0	C
18	13	1.080	12	125.82	17	-123.94	0	H
19	17	1.080	12	124.69	13	-164.11	0	H
20	14	1.080	12	109.15	12	-155.59	0	H
21	14	1.080	13	111.86	12	91.25	0	H
22	16	1.080	15	109.97	14	-117.03	0	H
23	16	1.080	15	109.54	14	133.21	0	H
24	15	1.080	14	107.80	13	-105.91	0	H
25	15	1.080	14	108.12	13	144.51	0	H

(2-η^1-1,2-planar-cyclohexadiene)bisphosphine platinum, 104

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	0.000	2	0.00	3	0.00	0	XX
12	1	2.000	2	180.00	3	0.00	0	C
13	12	1.435	1	125.20	3	90.00	0	C
14	13	1.481	12	128.92	1	176.08	0	C
15	14	1.519	13	116.58	12	-17.80	0	C

$(2\text{-}\eta^1\text{-}1,2\text{-planar-cyclohexadiene})$bisphosphine platinum, 104-continued

16	12	1.435	13	109.59	14	-4.03	0	C
17	16	1.481	12	128.92	11	-176.08	0	C
18	13	1.080	12	118.01	11	0.92	0	H
19	16	1.080	12	118.01	11	0.92	0	H
20	14	1.080	13	111.08	12	-147.32	0	H
21	14	1.080	13	105.72	12	102.79	0	H
22	17	1.080	16	111.08	12	147.32	0	H
23	17	1.080	16	105.72	12	-102.79	0	H
24	15	1.080	14	109.66	17	110.89	-1	H
25	15	1.080	14	110.32	17	109.52	1	H

(6-η^1-bicyclo[3.1.0]hexan-6-ylidene)bisphosphine platinum, 109

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCS	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	0.000	2	0.00	3	0.00	0	XX
12	1	2.000	2	180.00	3	0.00	0	C
13	12	1.490	1	146.74	3	90.00	0	C
14	13	1.528	12	119.15	11	-69.90	0	C
15	14	1.532	13	106.22	12	-81.16	0	C

(6-η^1-bicyclo[3.1.0]hexan-6-ylidene)bisphosphine platinum, 109-continued

16	12	1.490	13	63.81	14	91.73	0	C
17	16	1.528	12	119.15	13	-91.73	0	C
18	13	1.080	12	121.14	11	95.51	0	H
19	16	1.080	12	121.14	11	-95.51	0	H
20	14	1.080	13	114.68	12	149.63	0	H
21	14	1.080	13	107.88	12	31.33	0	H
22	17	1.080	16	114.68	12	-149.63	0	H
23	17	1.080	16	107.88	12	-31.33	0	H
24	15	1.080	14	111.42	13	-89.77	0	H
25	15	1.080	14	113.35	13	155.18	0	H

$(\eta^2$-cycloheptatetraene)bisphosphine platinum

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	2.149	2	180.00	3	0.00	0	XX
12	11	0.730	1	90.00	3	0.00	0	C
13	11	0.730	12	180.00	1	0.00	0	C
14	13	1.342	12	142.59	1	145.65	0	C
15	14	1.468	13	116.88	12	16.42	0	C

(η^2-cycloheptatetraene)bisphosphine platinum-continued

16	15	1.360	14	125.39	13	-31.75	0	C
17	16	1.468	15	128.64	14	1.22	0	C
18	17	1.350	16	130.30	15	24.27	0	C
19	12	1.080	13	125.77	14	-121.42	0	H
20	14	1.080	15	119.20	16	138.49	0	H
21	15	1.080	16	118.89	17	179.47	0	H
22	16	1.080	17	113.71	18	-155.22	0	H
23	17	1.080	18	117.44	12	176.16	0	H
24	18	1.080	12	117.78	13	144.21	0	H

(η^1-cycloheptatrienylidene)bisphosphine platinum

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	2.000	2	180.00	3	0.00	0	C
12	11	1.488	1	119.45	3	90.00	0	C
13	12	1.356	11	131.43	1	180.00	0	C
14	13	1.453	12	129.91	11	0.00	0	C
15	11	1.488	12	121.07	13	0.00	0	C

(η^1-cycloheptatrienylidene)bisphosphine platinum-continued

16	15	1.356	11	131.43	12	0.00	0	C
17	16	1.453	15	129.91	11	0.00	0	C
18	12	1.080	11	113.02	15	180.00	0	H
19	13	1.080	12	117.22	11	180.00	0	H
20	14	1.080	13	114.72	12	180.00	0	H
21	15	1.080	11	113.02	12	180.00	0	H
22	16	1.080	15	117.22	11	180.00	0	H
23	17	1.080	16	114.72	15	180.00	0	H

(7-η^1-bicyclo[4.1.0]hepta-2,4-dien-7-ylidene)bisphosphine platinum, 112

Name of Atom A	Name of Atom B	Rab Bond Distance	Name of Atom C	<ABC	Name of Atom D	<ABCD	Rotation Sense	
1	0	0.000	0	0.00	0	0.00	0	PT
2	1	1.000	0	0.00	0	0.00	0	XX
3	1	2.280	2	55.00	0	0.00	0	P
4	1	2.280	3	110.00	2	0.00	0	P
5	3	1.450	1	109.47	2	60.00	0	H
6	3	1.450	1	109.47	5	109.47	1	H
7	3	1.450	1	109.47	5	109.47	-1	H
8	4	1.450	1	109.47	2	60.00	0	H
9	4	1.450	1	109.47	8	109.47	1	H
10	4	1.450	1	109.47	8	109.47	-1	H
11	1	2.000	2	180.00	3	0.00	0	C
12	11	1.485	1	147.72	3	90.00	0	C
13	12	1.488	11	124.80	1	76.71	0	C
14	13	1.357	12	122.67	11	61.79	0	C
15	11	1.486	1	147.72	3	-90.00	0	C

(7-η^1-bicyclo[4.1.0]hepta-2,4-dien-7-ylidene)bisphosphine platinum, 112-continued

16	15	1.486	11	124.80	1	-76.71	0	C
17	16	1.355	15	122.67	11	-61.79	0	C
18	12	1.080	13	113.78	14	-143.95	0	H
19	15	1.080	16	113.78	17	143.95	0	H
20	13	1.080	14	121.68	17	-172.30	0	H
21	16	1.080	17	121.68	14	172.30	0	H
22	14	1.080	13	122.08	20	-5.83	0	H
23	17	1.080	16	122.08	21	5.83	0	H

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BIOGRAPHICAL SKETCH

William Randolph Winchester was born July 13, 1957, in Roswell, New Mexico. As his father was a pilot in the United States Air Force, his formative years were spent moving almost annually and living in nine different states.

In spring, 1979, he received a B.S. in chemistry/physics from New College in Sarasota, Florida. This had followed brief stints as a Robert A. Welch Fellow at Texas Christian University and as an Undergraduate Research Fellow at Argonne National Laboratory in Chicago, Illinois.

In fall, 1979, Randy entered graduate study at the University of Florida. As a graduate student he has held a University of Florida Fellowship from 1979 to 1981; won the Dupont Teaching award; held a Proctor and Gamble Fellowship; and worried often about ever finishing.

Mr. Winchester has accepted an NSF-NATO Fellowship to study with Professor Dr. P. v. R. Schleyer at the University of Erlangen-Nuremberg in February 1985.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones
Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

J. R. Sabin
Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

M. A. Battiste

M. A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier

W. R. Dolbier, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

N. Y. Öhrn
Professor of Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 1985

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